Lewis Acidity and Basicity: An Ab Initio Study of Proton and BF₃ Affinities of Oxygen-Containing Organic Compounds

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The gas phase proton and BF₃ affinities, PA and BF₃A, of seventeen oxygen bases, water (**1**), methanol (**2**), dimethyl ether (**3**), oxetane (**4**), tetrahydrofuran (**5**), 7-oxanorbornene (**6**), furan (**7**), formaldehyde (**8**), acetaldehyde (**9**), acetone (**10**), acrolein (**11**), 2-butenal (**12**), 3-methyl-2-butenal (**13**), 3-buten-2-one (**14**), methyl formate (**15**), methyl acetate (**16**), and methyl propenoate (**17**), have been determined by geometry optimization of all species at RHF/6-31G* level, addition of zero point energy corrections at the same level, and correlation energy corrections by single point calculations up at MP2/6-31G* and MP3/6-31G* levels. The predicted order of Lewis basicity and BF₃A values (in kJ mol⁻¹) at 298 K are the following: **7** (26) < **8** (34) < **1** (46) < **15** (48) < **9** (50) < **17** (53) < **11** (54) < **10** (58) ≈ **14** (58) ≈ **16** (58) < **12** (60) < **2** (65) < **13** (66) < **3** (71) < **6** (76) < **5** (82) < **4** (85). The predicted order of basicity toward H⁺ and PA values (in kJ mol⁻¹) at 298 K are the following: **7** (704) < **1** (707) < **8** (713) < **2** (766) < **9** (770) < **15** (784) < **3** (798) < **11** (803) < **10** (814) < **16** (822) < **4** (825) < **5** (832) < **12** (835) ≈ **14** (835) ≈ **17** (835) < **6** (848) < **13** (859). The factors which determine Lewis vs Lowry–Bronsted acidity/basicity are discussed.

Introduction

Nucleophilic substitution, elimination, and addition reactions paradoxically are often catalyzed by initial electrophilic attack on the substrate. The role of the electrophile is to form an intermediate complex with the substrate, thereby increasing the reactivity of the substrate toward the desired nucleophile. A number of typical examples involving oxygen bases are shown in Scheme 1. The efficiency of the catalysis depends on the basicity of the oxygen atom toward the particular Lewis acid, which in turn determines the equilibrium constant of the central complexation reaction. Scales of solvent Lewis basicity have been established from the measurement of complexation enthalpies, toward BF₃ and a number of other Lewis acids.[1] Some gas phase data are available.[2–6] Structural and/or spectroscopic data have been reported for BF₃ complexed to water,[7] 2-methylacrolein,[8] and benzaldehyde.[9] These will be discussed below in connection to the present study.

We examine here theoretically, the basicity of a variety of oxygen bases toward the Lewis acid BF₃ and draw the comparison to the equivalent reaction with proton. We are particularly interested in the effect of coordination of the oxygen (ether type oxygen vs carbonyl type oxygen) and on the effects of alkylation (water, alcohols, and ethers), geometric constraints (i.e. ring size in cyclic ethers), and conjugation (saturated and unsaturated

Scheme 1
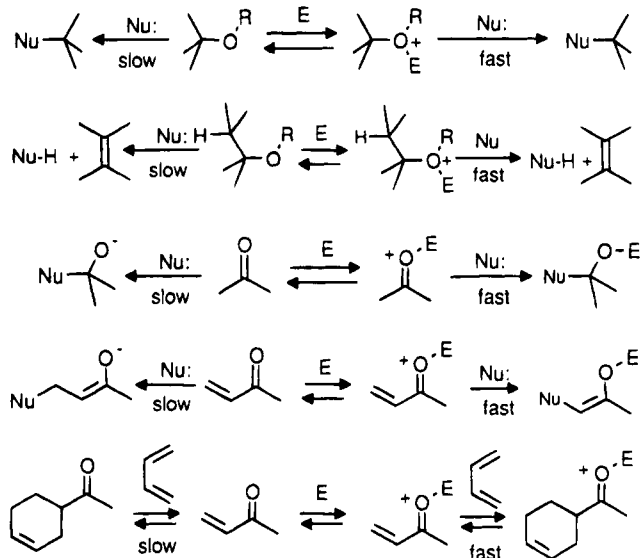
aldehydes, ketones, and esters). The last considerations are particularly important in Diels–Alder reactions[10,11] (the last reaction of Scheme 1) since both the reactant and product have basic sites. The normal use of solvents of low polarity, such as CH₂Cl₂, has the consequence that coordination of the "catalyst" to the substrate is essentially complete and use of stoichiometric amounts of the "catalyst" may actually influence the reactant/product distribution as was found for an intramolecular Diels–Alder reaction of a furan.[12]

Compounds **1–17** comprise our "basis set". We examine the structures and relative energies of the proton and BF₃ complexes of each of these. The complexes will be

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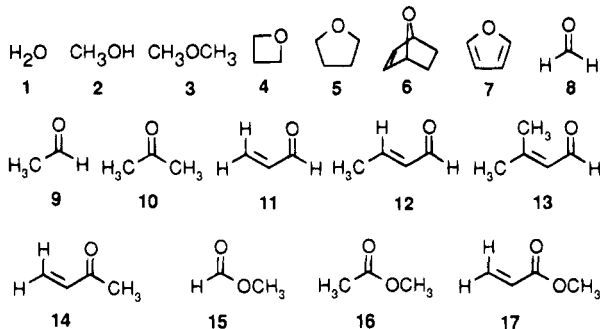(8) Corey, E. J.; Loh, T.-P.; Sarshar, S.; Azimioara, M. *Tetrahedron Lett.* **1992**, *33*, 6945–6948.

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denoted **1**–H⁺–**17**–H⁺ and **1**–BF₃–**17**–BF₃, with any required stereochemical labels.

H₂O   CH₃OH   CH₃OCH₃
1   **2**   **3**   **4**   **5**   **6**   **7**   **8**

9   **10**   **11**   **12**   **13**

14   **15**   **16**   **17**

Computational Methods

Theoretical. The geometries of BF₃, the oxy compounds, and their protonated and BF₃-complexed forms were fully optimized by Hartree–Fock SCF calculations at the 6–31G* level by using the GAUSSIAN 90[13] or GAUSSIAN 92[14] system of programs. In each case, the geometries were confirmed as stationary points by harmonic frequency analysis, which also provided corrections for zero point vibrational energies (ZPVE). For the latter purpose, ZPVE values were scaled by 0.89. Binding energies were taken as the difference between the energy of the H⁺ or BF₃ complex and the sum of the separate species. No account was taken of basis set superposition effects, which should be small[15] compared to binding energies and similar in isomeric structures. The effect of electron correlation on the binding energies was assessed by single point recomputation at the level of second and third order Møller–Plesset perturbation theory (MP2 and MP3).[16,17] For representative complexes with BF₃ (water **1**–BF₃, dimethyl ether **3**–BF₃, furan **7**–BF₃, formaldehyde **8**–BF₃, acetaldehyde **9**–(*E*)–BF₃, acrolein (*E*)–**11**–(*E*)–BF₃, and methyl formate **15**–(*E*)– BF₃ and **15**–(*Z*)–BF₃), complete optimization at the MP2/ 6–31G* level was carried out in order to investigate the effect of electron correlation on the structure and energies of the complexes.

Proton affinity, PA, is defined at 298 K as the enthalpy change of reaction 1, and the BF₃ affinity, BF₃A, in an

$$B{:}H^+ \rightarrow B{:} + H^+ \qquad + PA \qquad (1)$$

analogous manner, as the enthalpy change of reaction 2.

$$B{:}BF_3 \rightarrow B{:} + BF_3 \qquad + BF_3A \qquad (2)$$

We indicate our use of proton affinities and BF₃ affinities at 0 K by the symbols, PA₀ and BF₃A₀, respectively.

Temperature dependence for PA and BF₃A may be estimated by addition of the sum of the thermodynamic functions, $H^0 - H_0^0$, for reactions 1 and 2, which were evaluated by standard statistical thermodynamic methods based on the rigid rotor-harmonic oscillator model. For the purpose of evaluation of $H^0 - H_0^0$, all normal modes, including low-frequency torsional modes, are treated as harmonic vibrations. The lowest frequency modes occur for torsion about the O–B axis, or about C–C bonds to methyl groups.

Results and Discussion

The α,β-unsaturated carbonyl species, **11**, **14**, and **17**, have diastereomeric conformations of similar energy. These were considered separately, and are identified by the stereochemical labels, *E* and *Z*, depending on whether the C=C and C=O double bonds adopt a *transoid* or *cisoid* geometry, respectively. In the case of the esters **15**–**17**, only the *s*–*cis* (*Z*) conformation of the carbomethoxy group was considered since this is known to be about 20 kJ mol⁻¹ more stable than the *s*–*trans* conformation. Complexation by H⁺ or BF₃ yields further diastereomeric possibilities since for unsymmetrical carbonyl compounds, the complexed group may adopt a position in the plane *cis* or *trans* to one of the groups attached to the carbonyl. These are also considered separately and are designated by the stereochemical label, *E* or *Z*, depending upon whether the Lewis acid has a *transoid* or *cisoid* orientation relative to the group of higher priority, respectively. Additionally, in the case of BF₃ complexes, the rotational orientation about the O–BF₃ axis must be considered. The structures of all of the stable BF₃ complexes are collected in Figure 1. For the sake of brevity, the structures of the uncomplexed and protonated species are not shown. Complete structural information in the form of Gaussian Archive entries is available for all species considered as supplementary material.

Ab initio energies of all compounds are collected in Table 1. The binding energies of the complexes with H⁺ (proton affinity, PA₀) and BF₃ (BF₃ affinity, BF₃A₀), in the form of the enthalpy changes for the reactions 1 and 2 at 0 K, are listed in Table 2. Values of $H^0 - H_0^0$ at 298 K for each individual species are shown in Table 1. The appropriate sum, $\Sigma H_{298} = H^0 - H_0^0(B{:}) + H^0 - H_0^0(X) - H^0 - H_0^0(B{:}X)$, may be used to estimate PA and BF₃A at 298 K as PA = PA₀ + ΣH_{298} and BF₃A = BF₃A₀ + ΣH_{298}. Values of PA and BF₃A derived from the MP3 numbers are shown in parenthesis in Table 2. It is readily apparent that temperature dependence of BF₃A is negligible. It is approximately 6 kJ mol⁻¹ for PA, due mainly to the value of $H^0 - H_0^0(H^+) = 6.2$ kJ mol⁻¹ at 298 K.

In the case of the protonated species, with the exception of water, the largest values of the proton affinity at 0 K (PA₀) are obtained at the Hartree–Fock level. The effect of electron correlation is to reduce the magnitude of the predicted value. The MP3 values fall between the RHF and MP2 values. The calculated PA₀ of water, ~700 kJ mol⁻¹, is essentially independent of the level of electron correlation and is in good agreement with the

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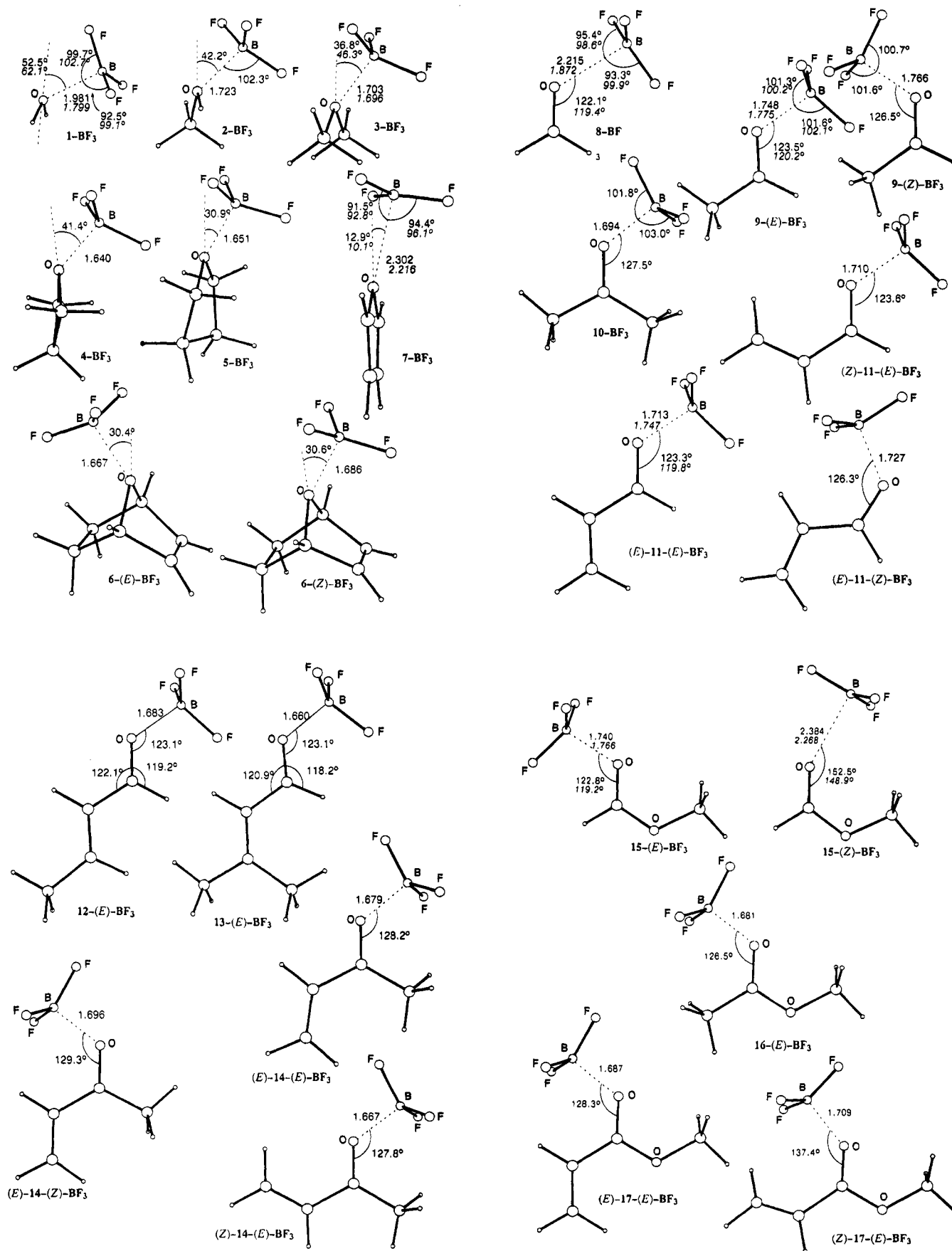
Figure 1. 3RHF/6-31G* optimized geometries of all BF$_3$ complexes. Numbers in italics are MP2/6-31G* optimized values.

experimental values, 694 kJ mol^{-1} (PA$_0$),[18] 700 kJ mol^{-1} (PA).[19] Comparison of PA values from Table 2, values

listed by Lias, et al.,[19] and the revised values of Szulejko and McMahon[20] reveals very good agreement in the

Table 1. Ab Initio Computational Results: Total Energies (Hartrees) and Zero Point Energies (kJ mol^{-1})

compound	RHF	ZPE^a	MP2^{b,c}	MP3^b	ΔE^d	$H^0_{298} - H^{0e}_0$
boron trifluoride, BF$_3$	−323.19549	35.0	−323.77704(−323.77866)	−323.77183		11.8(11.6^f)
water, H$_2$O, 1	−76.01075	60.3	−76.19597(−76.19685)	−76.20198		9.9
1−H$^+$	−76.28934	96.4	−76.47383	−76.48120		10.1
1−BF$_3$	−399.22055	103.8	−399.99346(−399.99736)	−399.99369		20.2
methanol, CH$_3$OH, 2	−115.03542	145.3	−155.34494	−115.36078		11.3
2−H$^+$	−115.33899	180.1	−115.64428	−115.66232		12.3
2−BF$_3$	−438.24890	188.6	−439.149466	−439.15966		21.7
dimethyl ether, 3	−154.06475	226.2	−154.50207(−154.50346)	−154.52683		14.0
3−H$^+$	−154.38238	261.8	−154.81314	−154.84098		15.5
3−BF$_3$	−477.27857	269.3	−478.30923(−478.31229)	−478.32814		25.1
oxetane, 4	−191.90938	246.9^g	−192.46961	−192.49776		13.4
4−H$^+$	−192.23868	283.0^g	−192.79058	−192.82183		13.9
4−BF$_3$	−515.12927	290.1	−516.28196	−516.30426		24.2
tetrahydrofuran, 5	−230.97645	330.6	−231.66856	−231.70500		15.7
5−H$^+$	−231.30799	366.4	−231.99217	−232.03205		16.5
5−BF$_3$	−554.19474	373.5	−555.47963	−555.51047		26.8
7-oxanorbornene, 6	−306.67556	365.4	−307.62116	−307.65906		16.0
6−(E)−H$^+$	−307.00798	400.7	−307.94555	−307.98794	0.0	16.9
6−(Z)−H$^+$	−307.01205	401.4	−307.94967	−307.99179	−10.1	16.9
6−(E)−BF$_3$	−629.89113	406.8	−631.42982	−631.46205	−5.5	27.7
6−(Z)−BF$_3$	−629.88974	405.9	−631.42736	−631.45962	0.0	28.2
furan, 7	−228.62521	198.8	−229.30749(−229.31033)	−229.32443		12.4
7−H$^+$	−228.90596	229.5	−229.57557	−229.60095		13.8
7−BF$_3$	−551.82878	236.2	−553.09658(−553.10131)	−553.10800		26.8
formaldehyde, 8	−113.86633	76.7	−114.16526(−114.16775)	−114.17170		10.0
8−H$^+$	−114.15643	115.0	−114.44283	−114.45384		10.2
8−BF$_3$	−437.07326	117.4	−437.95790(−437.96312)	−437.95854		22.2
acetaldehyde, 9	−152.91597	157.0	−153.34455(−153.34692)	−153.36033		12.9
9−(E)−H$^+$	−153.22612	193.4	−153.64291	−153.66385	−2.0	13.4
9−(Z)−H$^+$	−153.22541	193.6	−153.64219	−153.66319	0.0	13.3
9−(E)−BF$_3$	−476.12621	198.9	−477.14282(−477.14628)	−477.15352	−6.4	24.4
9−(Z)−BF$_3$	−476.12321	198.9	−477.14054	−477.15108	0.0	24.4
acetone, 10	−191.96224	236.1	−192.52161	−192.54672		16.9
10−H$^+$	−192.28784	271.3	−192.83560	−192.86635		17.2
10−BF$_3$	−515.17371	277.6	−516.32214	−516.34243		28.0
acrolein, (Z)−11	−190.75977	174.6	−191.30626	−191.32500	0.0	14.2
(Z)−11−(E)−H$^+$	−191.08462	211.6	−191.61696	−191.64019	−14.5	14.4
(Z)−11−(Z)−H$^+$	−191.07797	211.2	−191.61126	−191.63452	0.0	14.8
(Z)−11−(E)−BF$_3$	−513.97169	216.4	−515.10546	−515.11918	0.0	25.6
(E)−11	−190.76242	174.5	−191.30849(−191.31162)	−191.32746	−6.5	14.2
(E)−11−(E)−H$^+$	−191.08735	211.7	−191.62072	−191.64365	−23.5	14.4
(E)−11−(Z)−H$^+$	−191.08679	211.9	−191.61947	−191.64260	−20.6	14.4
(E)−11−(E)−BF$_3$	−513.97403	216.4	−515.10817(−515.11219)	−515.12184	−7.0	25.6
(E)−11−(Z)−BF$_3$	−513.97111	216.3	−515.10598	−515.11932	−0.5	25.5
(E,E)-2-butenal, 12	−229.80397	253.7	−230.48111	−230.50890		18.1
12−(E)−H$^+$	−230.14065	289.9	−230.80536	−230.83710		18.6
12−(E)−BF$_3$	−553.01809	295.6	−554.28312	−554.30573		29.5
(E)-3-methyl-2-butenal, 13	−268.83916	332.8	−269.64971	−269.68604		22.1
13−(E)−H$^+$	−269.18431	368.0	−269.98232	−270.02279		22.8
13−(E)−BF$_3$	−592.05541	374.6	−593.45398	−593.48513		33.6
3-buten-2-one, (E)−14	−229.80591	253.5	−230.48324	−230.51171	0.0	18.0
(E)−14−(E)−H$^+$	−230.14089	288.9	−230.80608	−230.83891	0.0	18.8
(E)−14−(Z)−H$^+$	−230.14132	288.9	−230.80590	−230.83896	−0.1	18.8
(E)14−(E)−BF$_3$	−553.01702	294.8	−554.28371	−554.30698	−2.4	29.6
(E)−14−(Z)−BF$_3$	−553.01631	294.4	−554.28278	−554.30594	0.0	29.7
(Z)−14	−229.80631	253.0	−230.48378	−230.51172	−0.4	18.1
(Z)−14−(E)−H$^+$	−230.14264	288.1	−230.80656	−230.83956	−2.4	19.0
(Z)−14−(Z)−H$^+$	−230.13742	287.8	−230.80245	−230.83547	+8.1	19.2
(Z)−14−(E)−BF$_3$	−553.01872	294.3	−554.28447	−554.30766	−4.6	29.6
methyl formate, 15	−227.78942	177.4	−228.39298(−228.39663)	−228.40400	0.0	14.5
15−(E)−H$^+$	−228.10376	212.3	−228.69636	−228.71246	−18.7	15.4
15−(Z)−H$^+$	−228.09672	212.1	−228.68913	−228.70526	0.0	15.3
15−(E)−BF$_3$	−550.99917	218.1	−552.18974(−552.19435)	−552.19617	−15.5	26.3
15−(Z)−BF$_3$	−550.99553	215.7	−552.18396(−552.18936)	−552.18944	0.0	28.4
methyl acetate, 16	−266.83683	254.8^g	−267.56963	−267.59067		18.7
16−(E)−H$^+$	−267.16474^g	289.1^g	−267.88705^g	−267.91345		19.7
16−(E)−BF$_3$	−590.04861	295.8	−591.36998	−591.38652		30.2
methyl propenoate, (E)−17	−304.67977	271.2	−305.52979	−305.55424	0.0	20.2
(E)−17−(E)−H$^+$	−305.01508	305.8	−305.85243	−305.88199	−5.9	21.4
(E)−17−(E)−BF$_3$	−627.89044	311.4	−629.32840	−629.34820	−7.0	32.2
(Z)−17	−304.68067	271.1	−305.53123	−305.55523	−2.7	20.2
(Z)−17−(E)−H$^+$	−305.01106	305.0	−305.85013	−305.87948	0.0	20.9
(Z)−17−(E)−BF$_3$	−627.88763	311.0	−629.32597	−629.34541	0.0	32.1

^{a} Zero point energies at RHF/6-31G*. ^{b} Single point calculation at the RHF/6-31G* geometry. ^{c} Numbers in parentheses optimized at MP2/6-31G*. ^{d} Relative energy (MP3/6-31G*//HF/6-31G* + 0.89×ZPVE) of isomeric species, in kJ mol^{-1}. ^{e} Enthalpy change from 0 K to 298 K (see text). ^{f} Reference 19. ^{g} Reference 15.

Table 2. Ab Initio Proton and BF_3 Affinities (kJ mol^{-1}) of Minimum Energy Structures[a] at 0 K

compound	proton affinity, PA_0			BF_3 affinity, BF_3A_0		
	RHF	MP2	MP3[b]	RHF	MP2[c]	MP3[b]
water, H_2O, **1**	699.4	697.5	701.1(707)	30.0	46.1(49.8)	44.6(46)
methanol, CH_3OH, **2**	766.2	755.1	760.9(766)	39.9	64.8	63.6(65)
dimethyl ether, **3**	802.4	785.2	793.3(798)	40.9	71.9(72.0)	70.2(71)
oxetane, **4**	832.5(830.1)[d]	810.7	818.9(825)	56.7	85.4	83.7(85)
tetrahydrofuran, **5**	838.8(836.8)[d]	817.9	827.0(832)	52.8	82.3	81.3(82)
7-oxanorbornene, **6**-(E)	841.5	820.4	832.2(838)	47.0	77.3	76.1(76)
6-(Z)	852.2	831.3	842.3(848)	44.2	71.7	70.6(70)
furan, **7**	709.9	676.7	698.8(704)	19.1	29.5(30.2)	28.7(26)
formaldehyde, **8**	727.7	694.8	706.8(713)	25.0	35.9(38.8)	34.3(34)
acetaldehyde, **9**−(E)	782.1	751.1	764.7(770)	32.6	49.6(48.2)	50.0(50)
9−(Z)	780.0	749.0	762.7(769)	24.7	43.6	43.5(44)
acetone, **10**	823.7	793.2	808.0(814)	36.2	55.9	56.9(58)
acrolein, (Z)−**11**−(E)	820.1	783.0	794.8(801)	37.1	52.1	52.6(53)
(Z)−**11**−(Z)	803.0	768.4	780.2(786)	e	e	e
(E)−**11**−(E)	820.2	786.8	797.2(803)	36.2	53.3(51.4)	53.1(54)
(E)−**11**−(Z)	818.6	783.4	794.4(800)	28.6	47.6	46.5(47)
(E,E)-2-butenal, **12**−(E)	851.9	819.3	829.6(835)	42.8	59.4	59.5(60)
(E)-3-methyl-2-butenal, **13**−(E)	875.0	842.1	853.0(859)	48.5	65.5	65.5(66)
3-buten-2-one, (E)−**14**−(E)	848.0	816.2	827.9(833)	34.7	55.9	55.9(56)
(E)−**14**−(Z)	849.3	815.8	827.9(833)	33.9	53.8	53.6(54)
(Z)−**14**−(E)	852.0	816.4	829.7(835)	38.8	56.5	57.7(58)
(Z)−**14**−(Z)	838.4	805.7	819.0(824)	e	e	e
methyl formate, **15**−(E)	794.4	765.6	779.0(784)	32.4	46.7(45.0)	48.3(48)
15−(Z)	776.1	746.8	760.2(766)	25.0	33.7(34.0)	32.8(31)
methyl acetate, **16**−(E)	830.6	803.0	817.1(822)	37.4	55.9	57.7(58)
methyl propenoate, (E)−**17**−(E)	849.7	816.4	829.9(835)	35.2	52.0	53.5(53)
(Z)−**17**−(E)	837.4	807.3	821.3(827)	25.8	42.1	43.8(44)

[a] Includes ΔZPE (×0.89). [b] Values in parentheses are corrected to 298 K using $H_{298}^0 - H_0^0$ values from Table 1. For H$^+$, $H_{298}^0 - H_0^0 = 6.2$ kJ mol^{-1}, ref 19. [c] Values in parentheses are for MP2/6-31G* optimized geometries. [d] Reference 15; value includes correction for basis set superposition error. [e] Least stable diastereomer, not calculated.

majority of cases. These are (compound, calcd PA, exptl PA,[19] exptl PA[20]): **1**, 707, 697, 690; **2**, 766, 761, 760; **3**, 798, 804, 793; **4**, 825, 824, −; **5**, 832, 832, −; **9**, 770, 781, −; **10**, 814, 823, 810; **15**, 784, 790, 787; **16**, 822, 828, 816.

For the BF_3 complexes, inclusion of electron correlation leads to a 40−60% increase in the magnitude of the binding energy. In all cases, binding energies calculated at the MP3/6-31G* level of correlation on the RHF/6-31G* geometries (MP3/6-31G*//RHF/6-31G* level) are similar to the MP2/6-31G*//RHF/6-31G* values. Unless stated otherwise in the discussion below, cited binding energies for both H$^+$ and BF_3 complexes are the MP3 values. We discuss the results for the individual species, with emphasis on the BF_3 complexes, before attempting to make sweeping generalizations.

Water−BF_3 (1−BF_3). The structure of the complex between water and boron trifluoride is shown in Figure 1. At the HF/6-31G* level, the BF_3 moiety lies 52.5° out of the H−O−H plane at a distance of 1.981 Å and adopts an eclipsed orientation with respect to the O−H bonds. At the MP2/6-31G*-optimized level, the BF_3 moiety is closer to the oxygen atom (1.799 Å) and closer to the perpendicular orientation (62.1°) relative to the plane of the water molecule. The calculated binding energy is little affected by reoptimization at the MP2 level, being 44.6 kJ mol^{-1} (HF) and 49.9 kJ mol^{-1} (MP2). The C_s structure shown in Figure 1 is not very consistent with the findings of a joint experimental/theoretical investigation of the infrared spectrum of matrix isolated 1−BF_3 and ab initio calculations at the RHF/4-31G level.[7] With

the 4-31G basis set, the out of plane angle was found to be close to zero, and modest agreement was found between calculated (after scaling) and observed vibrational frequencies in the matrix isolation IR study. The present RHF/6-31G* vibrational frequencies, even after scaling by 0.89, differ by approximately 100 cm^{-1} for three modes, and 230 cm^{-1} for another, from the bands attributed to the 1:1 complex 1−BF_3. The MP2/6-31G* frequencies are somewhat closer.[21] However, even after scaling by 0.95, four modes still differ by approximately 100 cm^{-1}. We do not have an explanation of the discrepancies at this time.

Methanol−BF_3 (2−BF_3) and Dimethyl Ether−BF_3 (3−BF_3). The structure of the methanol complex (Figure 1) is not analogous to that found for 1−BF_3. The BF_3 moiety is predicted to be 42.2° out of the C−O−H plane at a shorter distance, 1.723 Å, and the B−F bonds adopt a more staggered geometry with respect to the O−H and O−C bonds. The trend toward smaller out-of-plane angles and shorter O−B distance continues with the ether complex, 3−BF_3, for which the out-of-plane angle is 36.8° and the O−B distance is 1.703 Å. 3−BF_3 has C_s symmetry with one B−F bond lying in the plane bisecting the C−O−C angle. Unlike the case of the water complex, the B−O separation is not much affected by MP2 optimization (1.696 Å), but as in 1−BF_3, the out-of-plane angle is greater, 46.3°.

Binding energies are predicted to be substantially larger than in the case of water, 63.6 kJ mol^{-1} and 70.2 kJ mol^{-1}, for 2−BF_3 and 3−BF_3, respectively. BF_3A of 3−BF_3 has been measured in the gas phase, 57.3 ± 0.8 kJ mol^{-1},[2,3] in disappointing agreement with the calcu-

(18) Pople, J. A.; Curtiss, L. A. *J. Phys. Chem.* **1987**, *91*, 155. Corrections to 0 K of data from ref 19.

(19) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, 23.

(20) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839−7848. See also, Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448.

(21) MP2/6-31G* vibrational frequencies of water−BF_3, in cm^{-1}, calcd (exptl, ref 7): a' 3711(3590), 1701(1725), 1390(1225), 857(863), 679(625), 619(460), 464(385), 287, 211; a'' 3834(3660), 1359(1240), 760-(818), 463, 271, 95.

lated value. However, the same technique yielded a value of 49.9 ± 1.2 kJ mol^{-1},[2] for the complex with diethyl ether, for which a higher value of 78.8 ± 0.4 kJ mol^{-1} [1] has been measured in methylene chloride solution.

BF$_3$ Complexes of Saturated Cyclic Ethers, 4−BF$_3$, 5−BF$_3$, 6-(E)-BF$_3$, and 6-(Z)-BF$_3$. The structures of the BF$_3$ complexes of oxetane (4), tetrahydrofuran (THF, 5), and 7-oxanorbornene (6) are shown in Figure 1. The oxetane and THF complexes, 4−BF$_3$ and 5−BF$_3$, have the shortest O−B separations of any of the complexes investigated in the present study, 1.640 and 1.651 Å, respectively. Modest out-of-plane angles of 41.4° and 30.9° are indicative of steric interactions of the *endo* fluorine atom and the α hydrogen atoms of the rings. The oxetane ring is folded by 10.0° in such a way as to place the BF$_3$ moiety into a quasiequatorial position and the *endo* fluorine atom between the more widely spaced quasiequatorial α hydrogen atoms. The bicyclic ether, 7-oxanorbornene, complexes with BF$_3$ to give two diastereomeric forms, designated for convenience (E) or (Z) depending on whether the BF$_3$ moiety is on the opposite side from the C=C double bond or on the same side, respectively (Figure 1). The more stable (by 5.5 kJ mol^{-1}) complex, 6-(E)-BF$_3$, has similar structural characteristics to the furan complex, whereas the less stable (Z) diastereomer has a somewhat longer B−O separation (1.686 Å vs 1.667 Å). It is of interest that the relative energies of the (E) and (Z) H$^+$ complexes are reversed, the proton preferring the side adjacent to the C=C double bond by 10.1 kJ mol^{-1}. Since the H$^+$ result is as expected on the basis of the basicity of the double bond, the BF$_3$ result must be regarded as unusual, and points to an intrinsic difference between H$^+$ and BF$_3$ as Lewis acids. The orientation of the B−O bond, or more specifically, the orientation of the $\sigma_{BO}*$ orbital, precludes additional stabilization by a two-electron two-orbital interaction with the π_{CC} bond orbital. This interaction is possible for the proton case because of the nondirectional characteristic of the polarized (toward H) $\sigma_{OH}*$ orbital. The decreased stability of 6-(Z)-BF$_3$, relative to 6-(E)-BF$_3$, must be attributed to steric effects, or in the parlance of orbital interaction theory, to the dominance of four electron two-orbital repulsive interactions.

The binding energies of 4−BF$_3$, 5−BF$_3$, and 6-(E)−BF$_3$ are among the highest, 83.7 kJ mol^{-1}, 81.3 kJ mol^{-1}, and 76.1 kJ mol^{-1}, respectively. The experimental value for 5−BF$_3$, measured in the gas phase,[3,5] is 78.6 ± 0.8 kJ mol^{-1}, in satisfactory agreement with the calculated value, corrected to 298 K, 82 kJ mol^{-1} (Table 2). Attempts to measure BF$_3$A for 4−BF$_3$ were unsuccessful due to rapid decomposition.[5]

The proton affinities of the two cyclic ethers 4 and 5 have been previously calculated at a similar level[15] and are in substantial agreement with the present values and experiment (see above).

Furan−BF$_3$ (7−BF$_3$). Furan 7 and its BF$_3$ complex 7−BF$_3$ were investigated at both RHF and MP2 levels. The results are essentially independent of the inclusion of electron correlation. The furan−BF$_3$ complex has the longest B−O bond (RHF 2.302 Å, MP2 2.216 Å), smallest out-of-plane angle (RHF 12.9°, MP2 10.1°), and weakest binding energy, 28.7 kJ mol^{-1}, of any of the BF$_3$ complexes of the present investigation. Again, this result is intrinsically different from the proton case. For furan, PA$_0$ is calculated to be essentially the same as that of water, whereas BF$_3$A$_0$ is less than that of water by 16 kJ mol^{-1}.

Conformations of Carbonyl Complexes. The BF$_3$ attaches to the oxygen atom and adopts a position in the plane of the carbonyl group, either *syn* or *anti* to a substituent on the carbonyl, and making a C−O−B angle of approximately 120°. In this respect the binding of BF$_3$ to a carbonyl oxygen is entirely analogous to that of a proton.[22] The orientation of the BF$_3$ group with reference to the O−B axis is such as to place a single fluorine atom in the (local) symmetry plane, either *syn* or *anti* to the carbon atom of the carbonyl group. In other words, the F−B−O−C dihedral angle is (approximately) equal to 0° or 180°, respectively. One of these orientations is a local minimum in the potential curve for hindered rotation about the O−B bond; the other corresponds to a transition structure for the rotation, and the energy difference between the two, to the energy barrier hindering rotation. The value of this barrier was determined for a number of the complexes. It was invariably less than 4 kJ mol^{-1}.

BF$_3$ Complexes of Formaldehyde (8), Acetaldehyde (9), and Acetone (10). For aldehydes, the preferred position for the BF$_3$ group is *syn* to the H atom (the (E) orientation), with the in-plane F atom in the *syn* position. In the BF$_3$−acetaldehyde complex, the *syn*-BF$_3$ isomer, 9-(E)−BF$_3$, is more stable than the *anti* (to H)-BF$_3$ isomer, 9-(Z)−BF$_3$, by 6.4 kJ mol^{-1}. In 9-(Z)−BF$_3$, where the BF$_3$ group is eclipsed to the methyl group, the preferred orientation of the BF$_3$ group places the in-plane F atom *anti* to C, i.e., in the sterically less hindered orientation. 9-(E)−BF$_3$ has C_s symmetry. Slight rotations of the CH$_3$ and BF$_3$ groups reduce the point group of the equilibrium geometry of 9-(E)−BF$_3$ to C_1. A similar effect is observed in 10−BF$_3$.

The formaldehyde−BF$_3$ complex 8−BF$_3$ has the second lowest binding energy, 34.3 kJ mol^{-1}, listed in Table 2, and also the second longest O−B separation, 2.215 Å. At the MP2/6-31G*-optimized level, this bond is substantially shorter, 1.872 Å, but the binding energy is raised by only 3 kJ mol^{-1} (Table 2). Comparison of the binding energies of 8−BF$_3$ and 9-(E)−BF$_3$, the latter being essentially unaffected by MP2 optimization, reveals that the presence of the single methyl group increases BF$_3$A by about 15 kJ mol^{-1}. Comparison of the energies of 9-(Z)−BF$_3$ and 10−BF$_3$ shows that the effect of the second methyl group on BF$_3$A is virtually the same as the first, an increase in magnitude by 16 kJ mol^{-1}. The effect of methylation on PA$_0$ values is not quite as additive, the first methyl group raising PA$_0$ by 58 kJ mol^{-1} (8−H$^+$ vs 9-(E)−H$^+$), the second by 47 kJ mol^{-1} (9-(Z)−H$^+$ vs 10−H$^+$).

The BF$_3$ Complexes of Acrolein (11). The *s-anti* form of acrolein, (E)-11, is more stable than the *s-syn* form, (Z)-11, by 6.5 kJ mol^{-1}. For each of these, the Lewis acid, H$^+$ or BF$_3$, may attach to either side of the carbonyl, generating four possible diastereomeric forms, (Z)-11-(E)-H$^+$, (E)-11-(E)-H$^+$, (Z)-11-(Z)-H$^+$, and (E)-11-(Z)-H$^+$, or (Z)-11-(E)-BF$_3$, (E)-11-(E)-BF$_3$, (Z)-11-(Z)-BF$_3$, and (E)-11-(Z)-BF$_3$. The *syn,syn* (Z,Z) diastereomer suffers the greatest steric crowding. Thus, *syn*-H$^+$ diastereomer of (Z)-11, (Z)-11-(Z)-H$^+$, is 14.5 kJ mol^{-1} less stable than the *anti*-H$^+$ form, (Z)-11-(E)-H$^+$, and more than 20 kJ mol^{-1} less stable than either protonated form of (E)-11 (Table 1). The three

(22) For reviews of binding of Lewis acids to carbonyl compounds, see: (a) Raber, D. J.; Raber, N. K.; Chandrasekhar, J.; Schleyer, P. v. R. *Inorg. Chem.* **1984**, *23*, 4076. (b) Shambayatti, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 256−272.

more stable BF_3 complexes were optimized (Figure 1). The most stable diastereomer, $(E)-11-(E)-BF_3$, is 6.5 kJ mol^{-1} more stable than $(E)-11-(Z)-BF_3$, in which the BF_3 group is buttressed against the vinylic C—H bond with virtually the same consequences as the BF_3—CH_3 interaction in the acetaldehyde complex. The computed structure of $(E)-11-(E)-BF_3$ is very close to the crystalline state and solution structures of 2-methylacrolein–BF_3,[8] and benzaldehyde–BF_3.[9] Comparison of the BF_3A_0 values of acrolein with those of acetaldehyde (Table 2) suggests that the stabilizing effect of a vinyl group attached to a carbonyl group is about the same as that of a methyl group for this property. This is in contrast to the relative influence on PA_0, for which the presence of the vinyl group rather than the methyl group results in an additional stabilization of about 30 kJ mol^{-1}.

The BF_3 Complexes of (E,E)-2-Butenal 12-(E),(E)-3-Methyl-2-butenal 13-(E), and 3-Buten-2-one (E)-14-(E). Compounds **12–14**, are derived from acrolein by the replacement of one or both hydrogen atoms of the terminal methylene group, or the aldehydic hydrogen atom, respectively, by a methyl group. Only the more stable complexes (with the proton or BF_3 group in the (E) orientation) were considered for **12** and **13**, and all except the least stable structure of the complexes of **14** were determined. Comparison of the BF_3A_0 values of these compounds with that of acrolein reveals an additive electronic contribution of each of the methyl groups of about 6 kJ mol^{-1}, in the absence of steric buttressing. In (E)-14-(E), where the steric interaction cannot be avoided, the stabilizing effect of replacement of the aldehydic hydrogen by a methyl group is 2.8 kJ mol^{-1}. A similar additivity is found in the PA_0 values, where each methyl group increases the value of PA_0 by about 32 kJ mol^{-1}.

The Complexes of Methyl Esters: Methyl Formate (15), Methyl Acetate (16), and Methyl Propenoate (17). The methoxy group of methyl esters adopts the *syn*-coplanar orientation relative to the carbonyl group, as shown in Figure 1. This orientation imposes a steric restriction on the coordination of BF_3 to that side of the carbonyl. Thus, the C—O—B angle and O—B distance of 15-(E)-BF_3 have typical values of 122.8° and 1.740 Å, whereas the corresponding values for 15-(Z)-BF_3 are 152.5° and 2.384 Å, and the former is more stable than the latter by 15.5 kJ mol^{-1}. None of these values is significantly altered upon reoptimization at the MP2/6-31G* level. Comparison of the binding energy of 15-(E)-BF_3 (48.3 kJ mol^{-1}) with that of the analogous acetaldehyde complex, 9-(E)-BF_3 (50.0 kJ mol^{-1}) and acrolein complex, $(E)-11-(E)-BF_3$ (53.1 kJ mol^{-1}), reveals that the extra stabilization toward complexation of BF_3 due to the presence of the methoxy group is about the same as that due to the methyl group or a vinyl group. On the other hand, PA_0 of methyl formate (15) is about 8 kJ mol^{-1} less than PA_0 of acrolein (11) and 14 kJ mol^{-1} greater than acetaldehyde (9). Similarly, BF_3A_0 of methyl acetate (16), acetone (10), and 3-buten-2-one (14) are predicted to be within 1 kJ mol^{-1}, with acetone having the smallest value. The value actually decreases by 4.2 kJ mol^{-1} when a vinyl group and methoxy group are both present, as in methyl propenoate (methyl acrylate) (17). The coordination energy of BF_3 to **17** has been calculated[10] at somewhat lower level to be 78 kJ mol^{-1}, without correction for ZPE contributions, which we find to be substantial, reducing the values of PA and BF_3A by about 30 and 10 kJ mol^{-1}, respectively. A value of 865 kJ mol^{-1} was calculated for the proton binding

energy at the same level.[10] After correction for ZPE, the value, 834 kJ mol^{-1}, is similar to the present MP3 value of PA_0. The prediction of a larger binding energy for the BH_3 complex compared to the BF_3 complex is probably correct and suggests that care should be exercised when using BH_3 as a model of BF_3.

General Observations and Conclusions

Effect of Correlation on PA and BF_3A. Proton affinities can be calculated quantitatively by high level correlated theories, such as G2.[18,23] Even with the more approximate procedure used here (RHF/6-31G* with single point corrections at MP2/6-31G* and MP3/6-31G* level + ZPE), values of PA are usually within 10 kJ mol^{-1} of the experimental values. The largest values are obtained at the RHF level. The MP2 estimate of the correlation energy leads to a 20 to 30 kJ mol^{-1} lowering of PA. This represents an over correction, since the MP3 value is midway between the two or even closer to the RHF value. Consequently, both the RHF and MP3 values are in good agreement with experimental values where the comparison can be made.

The effect of electron correlation on the binding energy of the BF_3 complexes (BF_3A) is qualitatively different from its effect on PA. As seen in Table 2, the RHF procedure consistently yields values of BF_3A of dicoordinated (ether) oxygen which are about 65% of the MP2 or MP3 values. For the carbonyl complexes, the RHF binding energy is about 70% of the MP2 or MP3 values. Binding energies calculated by the two correlated methods are usually within 1 kJ mol^{-1} of each other. Complete optimization of the structures of representative species at the MP2 level resulted in modest changes except in the case of the water and furan complexes (see above). However, except for these complexes where the discrepancy between single point and optimized MP2 binding energies was 3–4 kJ mol^{-1}, the effect of geometry reoptimization on the BF_3A value is less than 2 kJ mol^{-1}. There are few opportunities for comparison of the predicted BF_3A values to experimental values. The most complete listing of the enthalpies of BF_3 complexation to a variety of Lewis bases is that of Maria and Gal[1] for the process,

$$B:BF_3 \text{ (soln)} \rightarrow B: \text{ (soln)} + BF_3 \text{ (g)} \qquad (3)$$
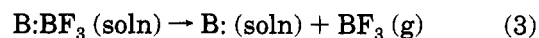
in CH_2Cl_2 solution. The enthalpy change of reaction 3 is comparable to BF_3A only to the extent that enthalpies of solution of the base and the complex are small enough to be neglected or similar enough to cancel. If one assumes that the heats of solution of the complex and the base differ approximated by the heat of solution of BF_3 itself (-10.0 ± 3.0 kJ mol^{-1}), then the estimated "experimental" BF_3A values of the five compounds which are common to the two studies are in the same order and fall within 11 kJ mol^{-1} of each other, the theoretical values being systematically lower.

Lewis Basicity of Ether Oxygen (BF_3A). Binding of BF_3 to water is predicted to be the weakest of the dicoordinated oxygen atom species examined, at 46 kJ mol^{-1}. If methanol is typical, binding to alcohols is predicted to be about 20 kJ mol^{-1} stronger. Binding to acyclic (unstrained) ether oxygen is predicted to be 6–7 kJ mol^{-1} stronger still, near 71 kJ mol^{-1}, based on the

(23) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1991,** *95,* 10549.

calculations on dimethyl ether. We expect BF$_3$A of diethyl ether to be similar in magnitude or smaller, since the gas phase value has been estimated to be 7.5 kJ mol^{-1} smaller.[2] This is an important consideration since BF$_3$ is typically available as a 1:1 complex with diethyl ether. The binding to tetrahydrofuran (THF), another common solvent, is 11 kJ mol^{-1} stronger than to dimethyl ether and has been measured to be 11.6 kJ mol^{-1} stronger than the binding to diethyl ether in CH$_2$Cl$_2$.[1] That this increase may be partly due to enhanced angle strain is suggested by the results for oxetane, for which the strongest binding of the present series is calculated, 85 kJ/mol. The complexation enthalpy for tetrahydropyran, in which angle strain should not be a consideration, has been measured to be 6 kJ mol^{-1} less than that of THF.[5] The bicyclic ether, 7-oxanorbornene (**6**), was selected as part of the present study because it forms a structural unit of the product of the intramolecular Diels−Alder reactions of interest in our laboratory.[12] The two binding sites for BF$_3$ are designated (*E*)-BF$_3$ (*anti* to the double bond) and (*Z*)-BF$_3$ (*syn* to the double bond). The (*E*)-BF$_3$ site is preferred by about 6 kJ mol^{-1}. The bicyclic molecule which incorporates the THF unit is less strongly complexed (76 kJ mol^{-1}) than THF itself (82 kJ mol^{-1}). The difference must be attributed to steric effects, which have been recognized to be particularly important for binding of BF$_3$ to Lewis bases[1] and which were seen above to be important for determining the relative stabilities of diastereomeric complexes of BF$_3$ with carbonyl compounds. We discuss this point further below.

Binding of BF$_3$ to Carbonyl Oxygen. Binding to the carbonyl group of aldehydes and ketones is examined in the series, formaldehyde (**8**), acetaldehyde (**9**), acetone (**10**), and the effect of α,β-unsaturation may be deduced from comparison to acrolein (**11**) and butenone (**14**). The effect of increased methylation in the carbonyl series is very similar to that calculated for the "ether" series, namely a large enhancement of binding due to a single methyl group (15 kJ/mol), and a modest further increase (6 kJ/mol) with the second. The electronic effect of addition of the second methyl group to the carbonyl may separated from the counterproductive steric interactions by comparison of the binding at the (*Z*)-BF$_3$ site of acetaldehyde and acetone. The difference, about 14 kJ mol^{-1}, is significantly larger than the calculated change for binding to "ether" oxygen (methanol vs dimethyl ether).

Order of Lewis Basicity (BF$_3$A) vs Affinity for Proton (PA). The calculated order of Lewis basicity, as measured by BF$_3$ affinity of the compounds studied (Table 2) is (least basic first, most basic last) the following: **7** < **8** < **1** < **15** < **9** < **17** < **11** < **10** ≈ **14** ≈ **16** < **12** < **2** < **13** < **3** < **6** < **5** < **4**. It is clear that there is no simple categorization by functional group since substitution plays an important role. Among the fully substituted compounds (no hydrogen atoms attached to C=O or −O−), but including alcohols and saturated aldehydes, one has the following order: **7** < **9** < **17** < **10** ≈ **14** ≈ **16** < **2** < **3** < **6** < **5** < **4**. This implies the order by functionality: furans < aldehydes < unsaturated esters < ketones ≈ vinyl ketones ≈ saturated esters < alcohols < acyclic ethers < cyclic ethers. The calculated order of basicity toward proton (Lowry−Bronsted basicity) is the following: **7** < **1** < **8** < **2** < **9** < **15** < **3** < **11** < **10** < **16** < **4** < **5** < **14** ≈ **17** ≈ **12** < **6** < **13**. Significant differences between PA and BF$_3$A are apparent. The least basic substances are the same (furan, water,

formaldehyde), alcohols are considerably less basic toward proton in a relative sense, esters are also relatively weak, and the effect of unsaturation is relatively more important, especially if the double bond is substituted by alkyl groups. The most basic (toward proton) substance of the present study is **13**, an unsaturated aldehyde with two methyl groups in the β position on the C=C double bond.

Lewis Acidity of BF$_3$ Compared to H$^+$. A reasonable rationalization may be proffered based on two factors which can be treated by orbital interaction theory,[24] namely, the steric requirement and the degree of electronic demand, of the Lewis acid. By steric requirement, we mean the spatial extent of occupied molecular orbitals of the Lewis acid which undergo repulsive four-electron two-orbital interactions with occupied molecular orbitals of the base. The ability to form a stable complex means that the attractive two-electron two-orbital interaction between the lowest unoccupied molecular orbital (LUMO) of the Lewis acid and the highest (or higher) occupied molecular orbital(s); (HOMO) of the base dominates the repulsive steric interactions. The balance between the two determines the structure and stability of the complex. BF$_3$ and H$^+$ are both categorized as hard Lewis acids in standard texts.[25] Of course, "H$^+$", in this context, refers to a species, [H−X]$^+$, where X is a neutral base such as water. Its initial interaction with a reference base is through its LUMO, $\sigma_{HX}*$, a low-lying antibonding orbital highly polarized toward H and therefore resembling the 1s atomic orbital of hydrogen. However, once the proton is covalently bonded to the base, its steric requirements are minimal, since it has no occupied orbitals. The BF$_3$ group, on the other hand, acts through its LUMO, which


BF_3
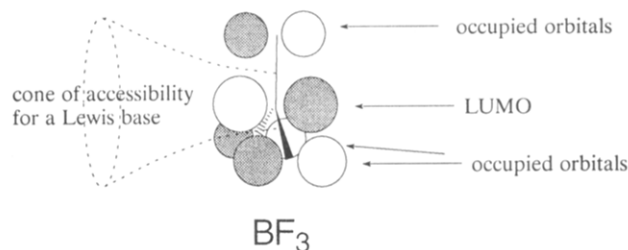
is for the most part a highly directed 2p orbital on the boron atom, surrounded by a ring of occupied 2p orbitals on the fluorine atoms. Steric repulsions are minimized and the attractive HOMO−LUMO interaction maximized if the base can accommodate itself into a narrow conical volume perpendicular to the face of the planar BF$_3$ moiety.

The "electronic demand" of the Lewis acid is more difficult to quantify, but conceptually easy to understand. In orbital interaction terms, it is the response of the occupied orbitals to accommodate the partial transfer of electron density that accompanies any HOMO−LUMO interaction. It is equivalent to the electrostatic effect due to the presence of a partial positive charge located at the base end (oxygen) of the covalent dative bond to the Lewis acid. The effect is present whether or not the Lewis acid itself bears a formal positive charge and is additional to any residual formal charge at the Lewis acid end of the bond. The electronic demand of the proton is trivially much greater than that of BF$_3$.

(24) Rauk, A. *The Orbital Interaction Theory of Organic Chemistry*; Wiley Interscience: New York, 1994; p 144.

(25) See, for example, March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985; p 229.

Lewis Basicity vs Lowry–Bronsted Basicity. The energy gained, and therefore the stability of the complex, depends primarily on the ability of the structure of the base to respond to the electronic demand of the Lewis acid, i.e. on the polarizability of the bond directly attached to the oxygen atom to which the Lewis acid is attached. This is equivalent to assessing the importance of the second (no bond) resonance structure:
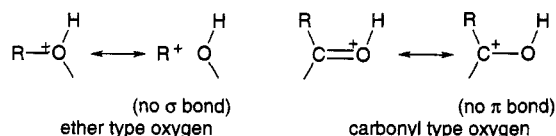
The importance of polarizability is greater when the electron demand is higher. The polarizability of the bond (σ or π) depends in turn on the ability of substituents to donate electrons into the σ_{OR}^* or π_{COH}^* orbitals. For alcohols or ethers, where R = alkyl, the polarizability of the bond is not high, hence the relatively low position of these substances in the order of Lowry–Bronsted basicity. However, the polarizability of the bond to oxygen can be increased substantially by substitution in R, as can be seen from the PA values of the homologous series of alcohols (R,PA);[19] Me, 761; Et, 788; iPr, 805; tBu, 810. The high basicity of the bicyclic ether **6** is readily understandable since the bonds to the bridging oxygen atom are allylic to the π bond, although the bond alignment is not the most favorable. In the case of protonated carbonyl compounds, the π donor ability of the R group itself will govern the basicity. The donor abilities of methyl, vinyl and methoxy groups are predicted to be virtually identical. Additional alkyl substitution on the vinyl group, however, greatly enhances the Lowry–Bronsted basicity (compound, PA): **11**, 803; **12**, 835; **13**, 859.

Being an electrically neutral moiety, the electronic demand of BF$_3$ is considerably less than that of the proton, and the energy gain from the ability of the base to respond is correspondingly less. Indeed, steric factors dominate in determining the stability of the complex. The HOMO of either the ether-type oxygen or the carbonyl oxygen is essentially a 2p orbital of the oxygen atom, aligned perpendicular to the plane of the substituents in the former case, and perpendicular to the C=O bond but lying in the plane of the carbonyl group in the latter case. Since the energy of the carbonyl HOMO is expected to be higher than that of the "ether" HOMO,[24] the intrinsic HOMO–LUMO interaction with BF$_3$ should be more favorable for the carbonyl case. That the stability of carbonyl complexes is *less* than of complexes with ether-type oxygen must be due to the unavoidable steric interaction in the former case, since the BF$_3$ group must be eclipsed to one or the other of the carbonyl substituents, but can adopt a staggered arrangement in bonding to ether-type oxygen.

Supplementary Material Available: Gaussian data (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.