Citation:

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

The gas phase proton and BF_3 affinities, PA and BF_3A, 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 BF_3A 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.

Figures:

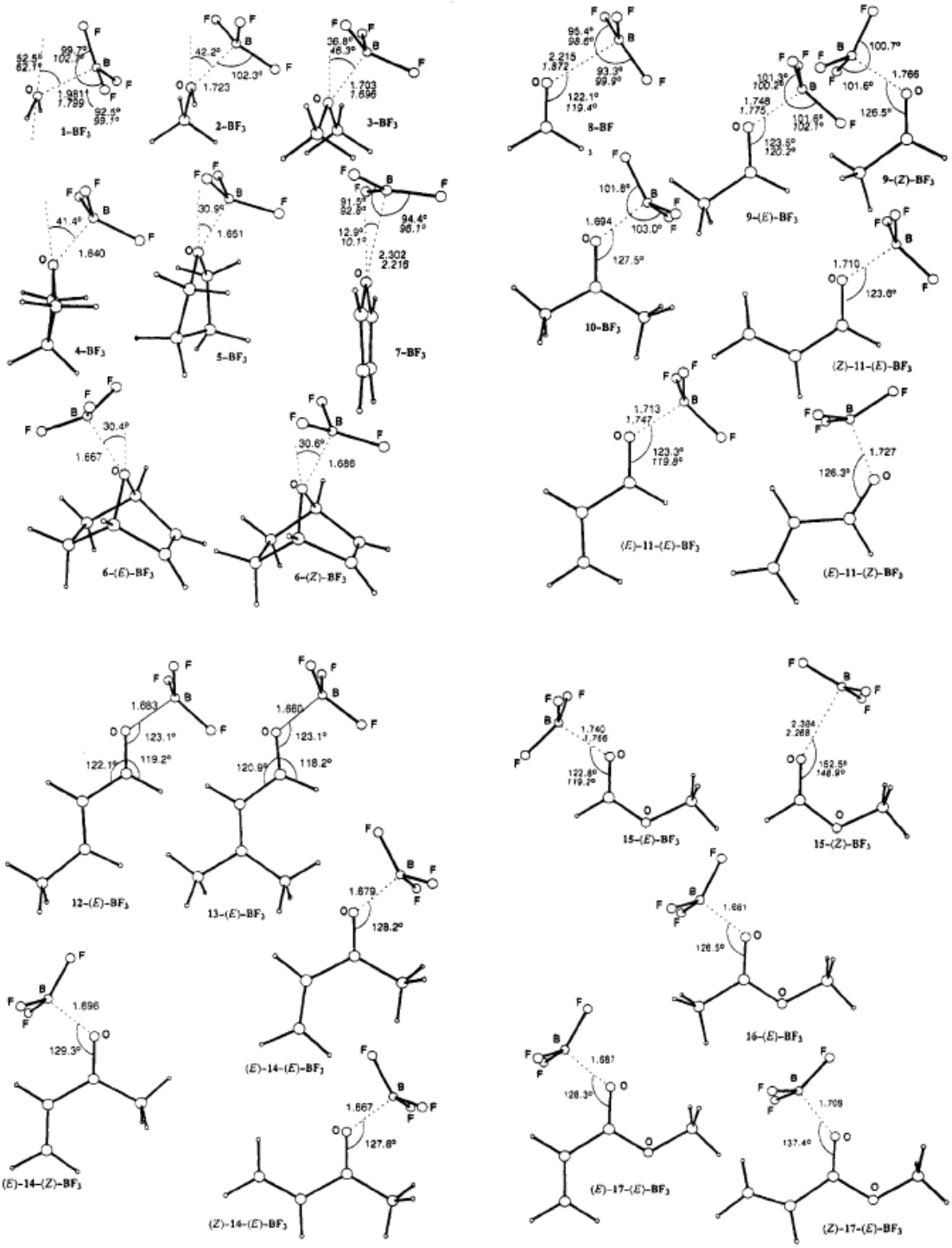


Figure 1. 3RHF/6-31G* optimized geometries of all BF_3 complexes. Numbers in italics are MP2/6-31G* optimized values.

Tables:

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	$H^0_{298} - H^0_0$[e]
boron trifluoride, BF_3	−323.19549	35.0	−323.77704(−323.77866)	−323.77183		11.8(11.6[f])
water, H_2O, **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_3OH, **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.

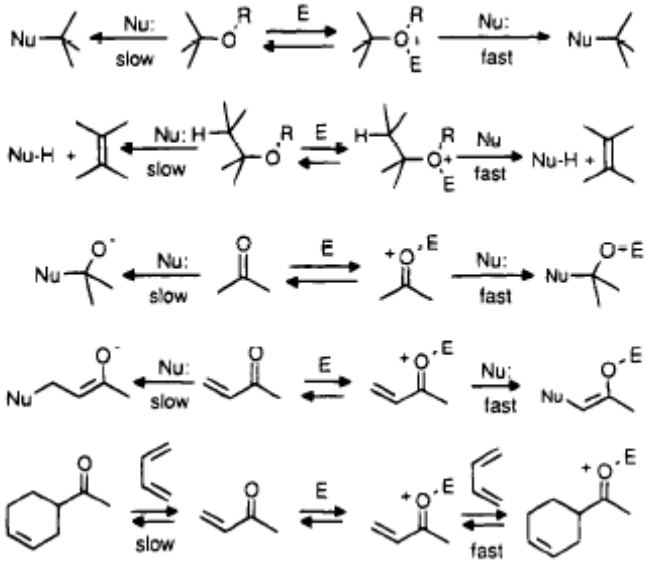
Table 2. Ab Initio Proton and BF_3 Affinities (kJ mol^{-1}) of Minimum Energy Structures[a] at 0 K

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 $H^0_{298} - H^0_0$ values from Table 1. For H^+, $H^0_{298} - H^0_0 = 6.2$ 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.

Schemes:

Scheme 1



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