Complexes of CO_2, COS, and CS_2 with the Super Lewis Acid BH_4^+ Contrasted with Extremely Weak Complexations with BH_3: Theoretical Calculations and Experimental Relevance[1]

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Abstract: Structures and energies of the complexes of CO_2, COS, and CS_2 with BH_4^+, a super Lewis acid (**1**−**4a**), were calculated with the density functional theory (DFT) at the B3LYP/6-311+G** level. Each of the complexes **1**−**4a** contains a hypercoordinate boron with a three-center two-electron (3c-2e) bond. Formation of **1**−**4a** from the complexation of CO_2, COS, and CS_2 with BH_4^+ was calculated to be exothermic by 26−42 kcal/mol. At the same B3LYP/6-311+G** level calculations indicate that complexation of CO_2, COS, and CS_2 with neutral BH_3 leads only to very weak complexes (**1**−**4c**) with relatively long B−O or B−S bonds. The computational results shed new light on related experimental studies of the ready and extremely mild superacid induced ionic hydrogenation of CO_2, COS, and CS_2 with $NaBH_4$ to methane.

Introduction

In preceding studies, one of us reported[2] the remarkable behavior of borohydride in superacids. Hydrogen−deuterium exchange studies prior to the liberation of hydrogen indicated protonation of BH_4^- to BH_5. The nature of BH_5 was extensively studied theoretically.[3,4]

In 1990, Olah and Wu observed[5] the mild ionic hydrogenation of CO_2, COS, and CS_2 with sodium borohydride/trifluoromethanesulfonic acid to methane. It was suggested that superacid protolytically activated the carbon oxides (sulfides) and thus facilitated the reaction with the hydrogen donor systems (such as borohydride and dihydrogen).

We recently reported[6] the calculated structures of the parent hexacoordinate boronium ion, BH_6^+, which can be considered as a complex of BH_4^+ with H_2 (Scheme 1). The reaction of BH_4^+ and H_2 to form BH_6^+ was calculated to be exothermic by 16.7 kcal/mol.[6] The reaction of BH_3 with H^+ to give BH_4^+ was calculated to be exothermic by as much as 137.9 kcal/mol.[6] BH_3 and BH_4^+ are isoelectronic with CH_3^+ and CH_4^{2+}, respectively. These calculations indicated that BH_6^+ can be formed by the reaction of BH_4^+ and H_2. As predicted, DePuy et al. were indeed able to prepare and observe the BH_6^+ experimentally in the gas phase by reacting BH_4^+ and H_2.[7,8] In comparison, the enthalpy of complexation of BH_3 and H_2 to give BH_5 is estimated to be exothermic by only 1.4 kcal/mol at 0 K and endothermic by 6.8 kcal/mol at room temperature.[3]

Scheme 1

BH_6^+ 　　　　 BH_4^+
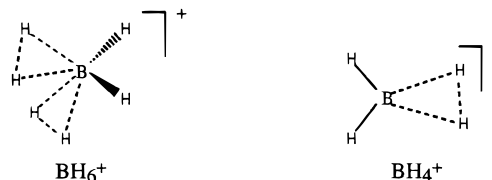
Lewis acid−base interactions are involved in many important catalytic reactions. Donor−acceptor complexes of the Lewis acid BH_3 have been the subject of many theoretical studies.[9] Anane et al. reported ab initio molecular orbital study of a series of donor−acceptor complexes of BH_3 including BH_3X (X = NH_3, PH_3, H_2O, and H_2S).[9a] Recently, we also reported[10] the ab initio calculated structures and energies of the B−H protonated H_3-BX^+ systems (X = NH_3, PH_3, OH_2, SH_2, and CO). Protonation of H_3BX to form H_4BX^+ was calculated to be highly exothermic. In continuation of our work we now report our study of the complexes of the BH_4^+ cation as well as neutral BH_3 with CO_2, COS, and CS_2 by the density functional theory (DFT) method.

Calculations

Calculations were carried out with the Gaussian 98 program system.[11] The geometry optimizations and frequency calculations were performed at the DFT[12] B3LYP[13]/6-311+G**[14] level. From calculated frequencies, the optimized structures were characterized as minima (number of imaginary frequencies (NIMAG) = 0). Final energies were calculated at the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE (B3LYP/

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Table 1.   Total Energies ($-$au) and ZPE[a]

	B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE (kcal/mol)		B3LYP/6-311+G**// B3LYP/6-311+G**	ZPE (kcal/mol)
H_4BOCO^+ (**1a**)	215.54320	31.5	H_3BSCS (**4c**)	861.17650	22.2
H_2BOCO^+ (**1b**)	214.34758	20.4	BH_3	26.62112	15.7
H_3BOCO (**1c**)	215.26992	24.9	BH_4^+	26.85011	21.3
H_4BOCS^+ (**2a**)	538.51306	29.9	CO_2	188.64692	7.0
H_2BOCS^+ (**2b**)	537.32288	18.9	COS	511.60013	5.5
H_3BOCS (**2c**)	538.22341	23.3	CS_2	834.55254	4.2
H_4BSCO^+ (**3a**)	538.50624	29.2	CO_2H^+ (**1d**)	188.85661	12.9
H_2BSCO^+ (**3b**)	537.31646	18.4	$SCOH^+$ (**2d**)	511.83612	11.4
H_3BSCO (**3c**)	538.22388	23.6	$OCSH^+$ (**3d**)	511.83936	10.1
H_4BSCS^+ (**4a**)	861.47245	27.7	CS_2H^+ (**4d**)	834.81312	8.8
H_2BSCS^+ (**4b**)	860.28574	17.1	H_2	1.17957	6.1

[a] Zero point vibrational energies (ZPE) at B3LYP/6-311+G**//B3LYP/6-311+G** scaled by a factor of 0.96.

Table 2.   Thermodynamics of the Dissociation of **1**$-$**4a**[a]

dissociation process	ΔH (kcal/mol)
$BH_4^+ + CO_2 \rightarrow BH_3 + CO_2H^+$ (**1d**)	+12.4
H_4BOCO^+ (**1a**) $\rightarrow BH_4^+ + CO_2$	+25.8
H_4BOCO^+ (**1a**) $\rightarrow H_2BOCO^+$ (**1b**) $+ H_2$	+5.1
H_3BOCO (**1c**) $\rightarrow BH_3 + CO_2$	−1.0
$BH_4^+ + COS \rightarrow BH_3 + SCOH^+$ (**2d**)	−4.1
$BH_4^+ + OCS \rightarrow BH_3 + OCSH^+$ (**3d**)	−7.4
H_4BOCS^+ (**2a**) $\rightarrow BH_4^+ + COS$	+36.3
H_4BOCS^+ (**2a**) $\rightarrow H_2BOCS^+$ (**2b**) $+ H_2$	+1.8
H_3BOCS (**2c**) $\rightarrow BH_3 + COS$	−0.7
H_4BSCO^+ (**3a**) $\rightarrow BH_4^+ + COS$	+32.7
H_4BSCO^+ (**3a**) $\rightarrow H_2BSCO^+$ (**3b**) $+ H_2$	+1.7
H_3BSCO (**3c**) $\rightarrow BH_3 + COS$	−0.8
$BH_4^+ + CS_2 \rightarrow BH_3 + CS_2H^+$ (**4d**)	−22.8
H_4BSCS^+ (**4a**) $\rightarrow BH_4^+ + CS_2$	+41.6
H_4BSCS^+ (**4a**) $\rightarrow H_2BSCS^+$ (**4b**) $+ H_2$	+0.1
H_3BSCS (**4c**) $\rightarrow BH_3 + CS_2$	−0.5

[a] At the B3LYP/6-311+G**//B3LYP/6-311+G** + ZPE level.

6-311+G**//B3LYP/6-311+G**) level. Calculated energies are given in Table 1. Calculated frequencies are given in Table 3.

Results and Discussion

Complexation of CO_2 with BH_4^+ leads to H_4BOCO^+ (**1a**) which was found to be a stable minimum at the B3LYP/6-311+G** level. The C_s symmetry structure **1a** contains a three-center two-electron (3c-2e) bond (Figure 1). The B$-$O bond distance of **1a** is 1.602 Å, 0.129 Å shorter than that found in H_3BOH_2 which indicates stronger B$-$O bonding in **1a** than in H_3BOH_2.[10] The O$-$C$-$O bond angle is 177.1°. The C$-$O (BH_4) and C$-$O bond distances of **1a** are 1.192 and 1.133 Å, respectively, 0.031 Å longer and 0.028 Å shorter than C$-$O of CO_2. This indicates that the ion **1a** may be considered as a resonace hybrid of the oxonium and oxocarbenium ions (Scheme 2).

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Table 3.   B3LYP/6-311+G** Calculated Frequencies and IR Intensities

no.	frequencies, cm^{-1} (IR intensities, KM/mol)
1a	48 (23), 146 (3), 527 (129), 600 (33), 636 (63), 684 (31), 712 (20), 827 (3), 948 (4), 1042 (11), 1093 (177), 1222 (18), 1382 (86), 1729 (27), 2475 (856), 2654 (2), 2776 (2), and 3454 (26)
1b	156 (5), 193 (0), 589 (64), 621 (40), 728 (184), 946 (40), 1037 (47), 1183 (139), 1346 (147), 2462 (709), 2703 (6), and 2890 (6)
2a	49 (29), 129 (9), 471 (1), 494 (40), 588 (127), 684 (6), 686 (16), 833 (4), 909 (35), 1004 (134), 1043 (11), 1104 (202), 1215 (12), 1705 (24), 1999 (1194), 2340 (8), 2750 (7), and 3499 (33)
2b	139 (7), 192 (1), 498 (29), 501 (1), 702 (111), 953 (46), 1040 (48), 1052 (310), 1206 (88), 1938 (1089), 2692 (21), and 2866 (18)
3a	124 (19), 146 (5), 461 (12), 474 (44), 524 (13), 527 (27), 605 (8), 714 (27), 780 (11), 849 (10), 1026 (4), 1061 (124), 1195 (6), 1665 (24), 2231 (505), 2635 (2), 2744 (0), and 3509 (44)
3b	159 (3), 307 (2), 496 (6), 503 (1), 574 (121), 695 (10), 830 (3), 949 (18), 1151 (67), 2259 (431), 2672 (2), and 2834 (2)
4a	112 (22), 132 (2), 378 (2), 427 (25), 499 (10), 521 (65), 600 (6), 623 (33), 745 (2), 814 (28), 1020 (2), 1055 (183), 1188 (8), 1553 (439), 1648 (23), 2629 (7), 2736 (1), and 3532 (60)
4b	145 (0), 276 (1), 428 (1), 432 (12), 601 (18), 611 (140), 813 (0), 949 (21), 1151 (106), 1552 (386), 2668 (9), and 2824 (4)

At the same B3LYP/6-311+G** level calculations indicated that complexation of CO_2 with neutral BH_3 leads only to a very weak complex, **1c**, with a long B$-$O bond of 2.556 Å. Both BH_4^+ and BH_3 contain an empty p-orbital which can formally accept an electron pair. However, only BH_4^+ forms (due to greater electrostatic attraction) a stronger B$-$O bond with the relatively poor base such as CO_2. Consequently BH_4^+ can be classified as a super Lewis acid, being a significantly stronger electron acceptor than BH_3.

As mentioned the ion BH_4^+ has been observed[7,8] in the gas phase, and its formation by protonation of BH_3 was calculated to be exothermic by 137.9 kcal/mol.[6] Our present calculations show that the formation of **1a** from the reaction of BH_4^+ and CO_2 is also exothermic by 25.8 kcal/mol (Scheme 3, Table 2). In comparison, formation of **1c** from BH_3 and CO_2 is endothermic by 1.0 kcal/mol (Table 2), and the formation of BH_6^+ from BH_4^+ and H_2 is exothermic by 16.7 kcal/mol.[6] BH_6^+ has indeed been recently observed by DePuy et al. in the gas phase by reacting BH_4^+ with H_2.[7,8] We have also considered possible proton transfer from BH_4^+ to CO_2 which was, however, calculated to be unfavorable by 12.4 kcal/mol (Table 2). The related dissociation of **1a** into **1b** and H_2 was also calculated to
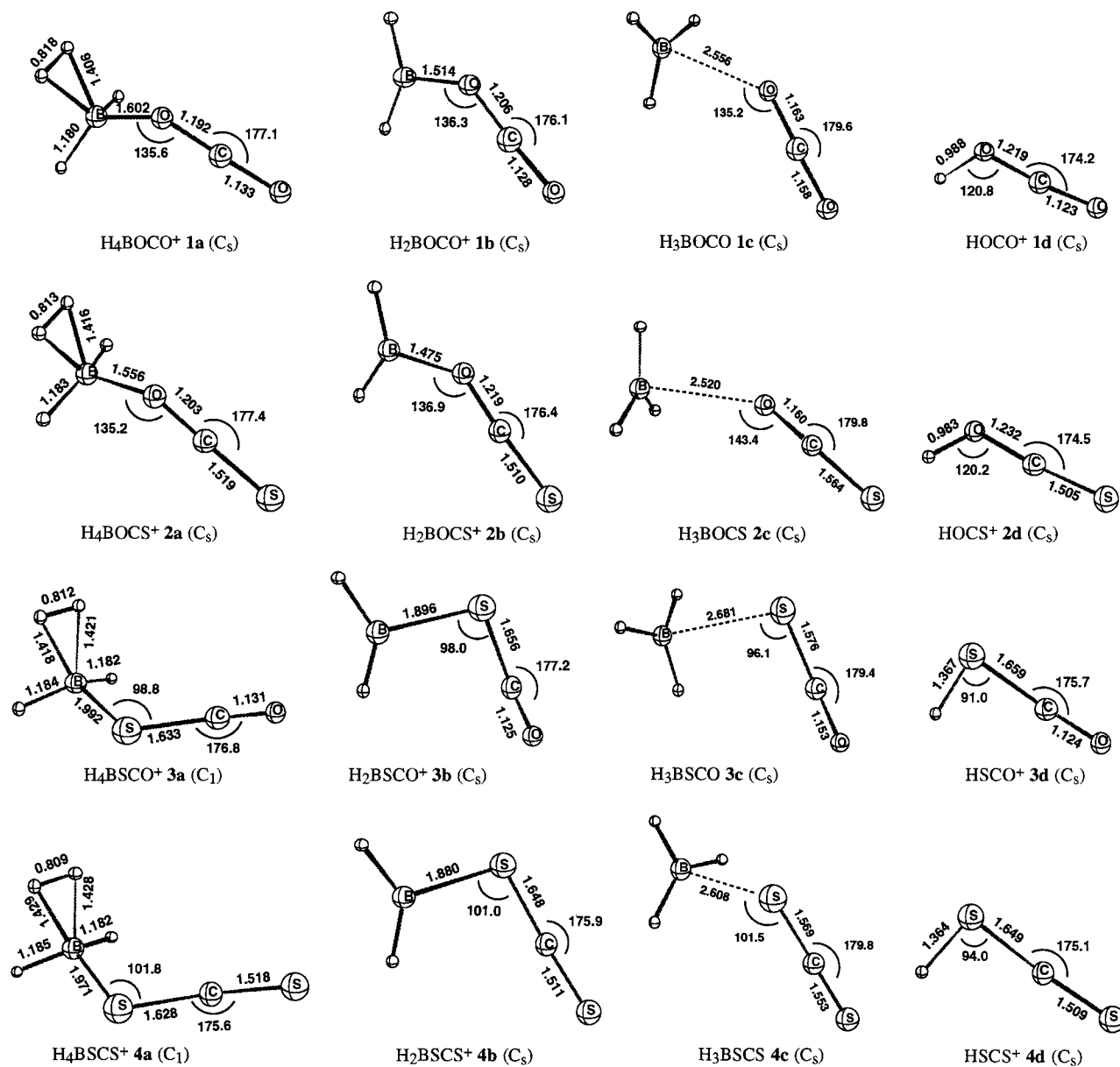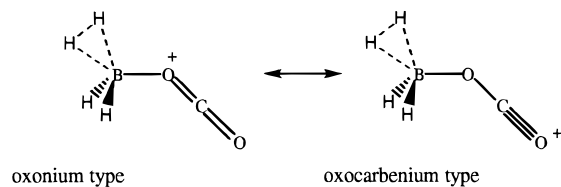
**Figure 1.** B3LYP/6-311+G** optimized structures of **1−4**.

Scheme 2

Scheme 3

be unfavorable by 5.1 kcal/mol (Scheme 4, Table 2). The planar structure **1b** can be considered as a complex of CO_2 with BH_2^+. These observations indicate that the complex **1a** is expected to be experimentally characterized in the gas phase.

Both O- and S-coordinated BH_4^+−COS complexes H_4-$BOCS^+$ (**2a**) and H_4BSCO^+ (**3a**), respectively, with 3c-2e bonds were found to be stable minima on the potential energy surface. The O-coordinated C_s symmetry structure H_4BOCS^+ (**2a**) is only 3.6 kcal/mol more stable than the S-coordinated C_1 symmetry structure H_4BSCO^+ (**3a**). This can also be rationalized on the basis of thermodynamic grounds: B−O bonds are stronger than B−S bonds. Formation of **2a** from BH_4^+ and COS were calculated to be exothermic by 36.3 kcal/mol (Scheme 3, Table
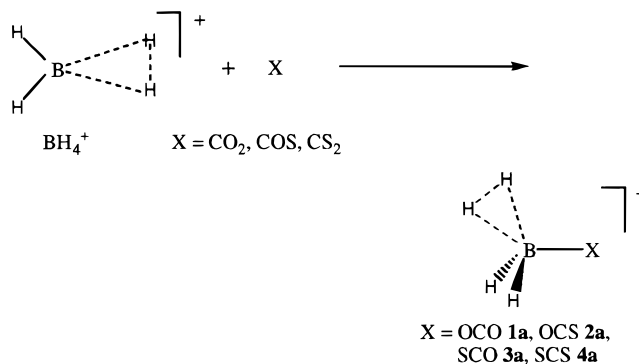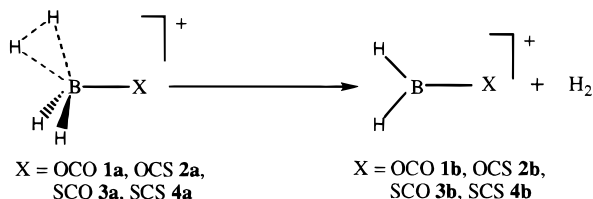
2). Dissociation of **2a** into **2b** and H_2 was calculated to be endothermic by only 1.8 kcal/mol. (Scheme 4, Table 2). This shows that if ion **2a** is formed, it will dissociate spontaneously into **2b** and H_2.

From the B3LYP/6-311+G** level of calculations it is apparent that complexations of O- and S-coordinated COS with

Scheme 4

X = OCO **1a**, OCS **2a**,
SCO **3a**, SCS **4a**

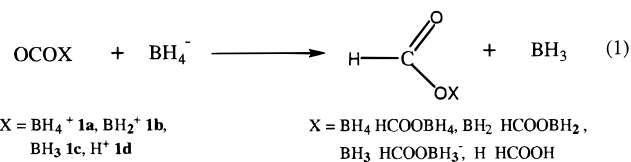X = OCO **1b**, OCS **2b**,
SCO **3b**, SCS **4b**

neutral BH_3 lead to very weak complexes **2c** and **3c** with long B–O (2.520 Å) and B–S (2.681 Å) bonds, respectively.

We have also calculated the structure of the BH_4^+–CS_2 complex H_4BSCS^+ (**4a**). The C_1 symmetry structure **4a** again contains a 3c-2e bond. The complexation of BH_4^+ and CS_2 to give **4a** was computed to be exothermic by 41.6 kcal/mol (Scheme 3, Table 2). Dissociation of **4a** into **4b** and H_2 is endothermic by only 0.1 kcal/mol (Scheme 4, Table 2). This indicates that, similar to **3a**, if ion **4a** forms, it will also spontaneously dissociate into **4b** and H_2. The interaction of neutral BH_3 with CS_2 leads to a very weak complex, **4c**, at the B3LYP/6-311+G** level with a long B–S (2.681 Å) bond.

Vibrational frequencies of the cations **1**–**4a** and **1**–**4b** were calculated at the B3LYP/6-311+G** level and are listed in Table 3. For comparison structures of protonated CO_2, COS, and CS_2 **1**–**4d** are also depicted in Figure 1. Francisco recently calculated the structure of protonated CO_2 at the CCSD(T)/6-311+G(3df,3pd) level.[15] The calculated bond lengths of C–O (H) and C–O are 1.228 and 1.126 Å, respectively, and agree very well with our calculated values of 1.219 and 1.123 Å.

The relative hydride affinities of **1a**–**d** were calculated by using the isodesmic reaction shown in eq 1. For cations **1a** and **1b** the reactions are exothermic by 181.1 and 186.2 kcal/mol, respectively. On the other hand, for neutral **1c** the reaction is exothermic by only 24.1 kcal/mol. In comparison, for protonated CO_2 **1d** the reaction is exothermic by 195.9 kcal/mol.

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$$OCOX \quad + \quad BH_4^- \quad \longrightarrow \quad H-C \quad + \quad BH_3 \qquad (1)$$

X = BH_4^+ **1a**, BH_2^+ **1b**,
BH_3 **1c**, H^+ **1d**

X = BH_4 $HCOOBH_4$, BH_2 $HCOOBH_2$,
BH_3 $HCOOBH_3^-$, H HCOOH

The computational results also shed new light on related experimental studies. The reported[5] remarkable reactivity of $NaBH_4/CF_3SO_3H$ in reducing CO_2, COS, and CS_2 to methane at room temperature and atmospheric pressure may not be necessary due to protolytic activation of CO_2 (COS and CS_2) which may involve protonation of BH_4^- to BH_5 and BH_6^+ (in some equillibrium), the latter cleaving to BH_4^+ and H_2. BH_4^+ being a superacidic Lewis acid complexes CO_2 as well as COS and CS_2 and activates them for subsequent ionic hydrogenation.

Conclusion

Complexes of CO_2, COS, and CS_2 with BH_4^+ (**1**–**4a**) were found to be the stable minima at the density functional theory (DFT) B3LYP/6-31G** level of calculation. The optimized structures show that **1**–**4a** all contain a 3c-2e bond. Formation of ions **1**–**4a** from the complexation of CO_2, COS, and CS_2 with BH_4^+ were calculated to be exothermic by 26–42 kcal/mol. The possible dissociation energies of **1**–**4a** into **1**–**5b** and H_2 were also computed. Complexation of CO_2, COS, and CS_2 with neutral BH_3 leads to very weak complexes **1**–**4c** with long B–O or B–S bonds. It is indicated that the complex **1a** between CO_2 and BH_4^+ should be experimentally observable in the gas phase. The BH_4^+ complexes are significantly activated compared with their parents and readily undergo ionic hydrogenation.