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G2 Molecular Orbital Investigation of $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) Interactions

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Structures of protonated alane-Lewis base donor−acceptor complexes $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) as well as their neutral parents were calculated using ab initio method at the G2 level. All the monocations $H_4AlXH_3(YH_2)^+$ are Al−H protonated involving hypercoordinated alane with a three-center two-electron (3c-2e) bond and adopt the C_s symmetry arrangement. The G2 energetic results show that the protonated alane-Lewis complexes are more stable than the neutral ones. They also show that this stability decreases when descending in the corresponding periodic table column, from nitrogen (or oxygen) to arsenic (or selenium) atoms. The G2 calculated protonation energies of $H_3AlXH_3(YH_2)$ to form $H_4AlXH_3(YH_2)^+$ were found to be highly exothermic. The possible dissociation of the cations $H_4AlXH_3(YH_2)^+$ into $H_2AlXH_3(YH_2)^+$and molecular H_2 are calculated to be endothermic.

1. Introduction

For a long time Lewis acids have been known to act as catalysts in organic reactions. The types of reactions in which trivalent aluminum plays a catalytic role are many and varied.[1−10] Donor acceptor complexes of Lewis acid AlH_3 and AlX_3 have been the subject of many experimental and theoretical studies.[11−24] Recently, we reported a detailed ab initio molecular orbital studies of a series of donor−acceptor complexes of AlH_3.[25−28] We showed that the stability of these complexes does not depends on the charge transfer. We have also shown that the donor−acceptor interaction was note based on a simple HOMO−LUMO mixture. Recently, Olah et al.[29,30] reported ab initio calculated structures and energies of the B−H protonated H_3BX^+ systems (X = NH_3, PH_3, OH_2, SH_2, CO, CO_2, COS, and CS_2). They have found that the protonation of H_3BX to form H_4BX^+ was highly exothermic. On the other hand, Olah and Rasul[31] reported on the calculated structures and energies of the hexa-, hepta-, and octacoordinate alonium ions, AlH_6^+, AlH_7^{2+}, and AlH_8^{3+} and related AlH_4^+, AlH_5^{2+}, and AlH_6^{3+} ions. They have shown that the structure of AlH_4^+ is C_{2v} symmetrical with a three-center two-electron (3c-2e) bond. In this work, we have now extended our investigation to the structures and energetics of protonated $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) as donor−acceptor complexes by ab initio calculations. The relative stability of these protonated complexes are examined. The possible dissociation of the cations $H_4AlXH_3(YH_2)^+$ into $H_2AlXH_3(YH_2)^+$ and molecular H_2 are also examined. To the best of our knowledge, no comparative study of these complexes has been carried out.

2. Computational Details

Ab initio calculations were performed using the GAUSSIAN92 program.[32] The calculations were performed in the Windows environment on a 900 MHz Pentium III PC having 128 MB of RAM and above 20 GB of available disk storage space. Geometry optimizations were performed at the MP2(full)/6-31G(d) level.[33] For improved energy, the Gaussian-2 (G2) energies[34] were computed. The electronic structure have been done using the natural bond orbital (NBO)[35] partitioning analysis at the MP2(full)/6-31G(d) level. NBO's are the localized set of easily recognizable Lewis-like (σ and π bond, lone pair, and core) and non-Lewis (σ* and π* antibond and Rhydberg) orbitals, which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set.

3. Results and Discussion

Tables 1 and 2 list the most important optimized geometrical parameters of $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) complexes at the MP2(full)/6-31G(d) level of theory, respectively. Table 3 lists the calculated G2 complexation energies of AlH_4^+ with XH_3 and YH_2, charge transfer, and proton affinities of $H_3AlXH_3(YH_2)$ complexes. Table 4 lists the G2 calculated thermodynamics values for the dissociation process of $H_4AlXH_3(YH_2)^+$ complexes into $H_2AlXH_3(YH_2)^+$ and molecular H_2. For accurate comparison, we also reported in Table 4 the QCISD(T)/6-311++G(d,p)//MP2(full)/6-31G(d) + ZPE dissociation energies. In Table 5 we reported the entropies and thermal corrections to the internal energy for all species studied in this work.

Al−H protonation of the H_3AlXH_3 (staggered C_{3v} symmetry conformation) leads to C_s symmetry monocation $H_4AlXH_3^+$ which was calculated to be a stable structure at the G2 level of theory. It contains a five-coordinate aluminum atom with a three-center two-electron (3c-2e) bond (Figure 1). AlH_4^+ which is isostructural with $CH_4{2}^+$ and BH_4^+ is of C_{2v} symmetry and also contains a 3c-2e bond.[31] The Al-X bond lengths of $H_4AlXH_3^+$ (X = N, P, and As) are 2.020, 2.471, and 2.523 Å, 0.064, 0.074, and 0.07 Å shorter than found in H_3AlNH_3, H_3AlPH_3, and H_3AlAsH_3, respectively, at the same MP2(full)/6-31G(d) level of theory which indicate stronger Al−X bonding in $H_4AlXH_3^+$ than that in H_3AlXH_3. The complexation energies AlH_4^+ + XH_3 (X = N, P, and As) are −57.55, −39.85, and −36.24 kcal/mol for $H_4AlNH_3^+$, $H_4AlPH_3^+$, and $H_4AlAsH_3^+$ protonated complexes respectively, while they are only −26.56, −12.59, and

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TABLE 1: Selected MP2(full)/6-31G(d) Bond Lengths (Å) and Bond Angles (°) of $H_4AlXH_3^+$, H_3AlXH_3, and $H_2AlXH_3^+$ (X = N, P, and As) Compounds

compound	Al−X	Al−H	Al−H_2	X−H[a]	H−H	∠H_{Al}−Al−X	∠H−X−Al[a]
$H_4AlNH_3^+$	2.020	1.560	2.189	1.026	0.746	108.43	113.96
				1.028			110.71
H_3AlNH_3	2.083	1.606		1.020		111.35	99.44
$H_2AlNH_3^+$	2.017	1.560		1.028		109.20	112.6
				1.027			113.36
$H_4AlPH_3^+$	2.471	1.562	2.157	1.400	0.748	108.50	116.54
				1.401			112.47
H_3AlPH_3	2.545	1.601		1.405		97.28	118.48
$H_2AlPH_3^+$	2.474	1.562		1.401		110.07	114.25
				1.399			116.39
$H_4AlAsH_3^+$	2.523	1.562	2.148	1.515	0.749	108.20	118.06
				1.517			112.36
H_3AlAsH_3	2.593	1.600		1.524		97.26	119.90
$H_2AlAsH_3^+$	2.525	1.563		1.516		108.70	117.44
				1.514			115.13

[a] The second value corresponds to equivalent hydrogen atoms.

TABLE 2: Selected MP2(full)/6-31G(d) Bond Lengths (Å) and Bond Angles (°) of $H_4AlYH_2^+$, H_3AlYH_2, and $H_2AlYH_2^+$ (Y = O, S, and Se) Compounds

compound	Al−Y	Al−H[a]	Al−H_2	Y−H	H−H	∠H_{Al}-Al−Y[a]	∠H−Y−Al
$H_4AlOH_2^+$	1.916	1.555	2.235	0.980	0.745	105.50	125.15
H_3AlOH_2[b]	2.051	1.607		0.974		98.89	113.40
		1.599				97.72	
$H_2AlOH_2^+$	1.908	1.556		0.981		105.80	125.35
$H_4AlSH_2^+$	2.414	1.559	2.146	1.343	0.748	106.86	102.23
H_3AlSH_2[b]	2.555	1.599		1.340		98.70	101.23
		1.597				95.69	
$H_2AlSH_2^+$	2.401	1.559		1.343		107.10	103.74
$H_4AlSeH_2^+$	2.523	1.560	2.161	1.483	0.748	107.31	96.92
H_3AlSeH_2[b]	2.642	1.600		1.479		99.75	98.36
		1.699				95.87	
$H_2AlSeH_2^+$	2.514	1.561		1.483		108.02	98.03

[a] The second value corresponds to equivalent hydrogen atoms. [b] From ref 26.

TABLE 3: G2 Complexation Energies E_{Comp} (kcal/mol) of Ligands (L = XH_3 and YH_2) with AlH_4^+ and AlH_3, Charge Transfer Qc(electron), and Proton Affinities PA (kcal/mol) of H_3AlL Complexes

complex	E_{comp}[a]	Qc[b]	PA[c]
$H_4AlNH_3^+$	−57.55(−26.56)	0.19(0.13)	208.26
$H_4AlPH_3^+$	−39.85(−12.59)	0.37(0.14)	203.63
$H_4AlAsH_3^+$	−36.24(−9.97)	0.37(0.24)	202.64
$H_4AlOH_2^+$	−46.82(−16.71[d])	0.15(0.12[d])	206.48
$H_4AlSH_2^+$	−34.76(−10.66[d])	0.30(0.19[d])	200.46
$H_4AlSeH_2^+$	−34.97(−9.74[d])	0.34(0.22[d])	201.60

[a] $E_{comp} = E(H_4AlL^+) - [E(H_4Al^+) + E(L)]$ with L = XH_3 (X = N, P, and As) and L = YH_2 (Y = O, S, and Se). The reported values in parentheses correspond to the nonprotonated parents complexes. [b] Charge transfer from XH_3 (or YH_2) to AlH_4^+. [c] PA = $E[H_3AlXH_3(YH_2)] - E[H_4AlXH_3(YH_2)^+]$. [d] From ref 26.

−9.97 kcal/mol for H_3AlNH_3, H_3AlPH_3, and H_3AlAsH_3 corresponding non protonated ones, respectively. However, the complexation energy decreases for each group when descending in the corresponding periodic table column, from nitrogen to arsenic.

On the other hand, one can see, from the NBO-MP2(full)/6-31G(d) analysis (Table 3), that there is no correlation between charge transfer and the G2 complexation energy. For the most stable protonated complex $H_4AlNH_3^+$, the charge transferred is 0.19e, while for the less stable complex $H_4AlAsH_3^+$, this transferred charge is 0.37e. We note also the same trend for the non protonated complexes. Nevertheless, we notice that the increase of the transferred charge contributes to the stability of protonated $H_4AlXH_3^+$ (X = N, P, and As) complexes according to their non protonated homologous H_3AlXH_3, respectively.

TABLE 4: Thermodynamics (in kcal/mol) of the Dissociation Process of Protonated Complexes

	G2			QCI[a]
dissociation process	ΔE_0	ΔH_0	ΔG_{298}	ΔE_0
$H_4AlNH_3^+ \rightarrow H_2AlNH_3^+ + H_2$	5.08	5.13	−0.03	4.28
$H_4AlPH_3^+ \rightarrow H_2AlPH_3^+ + H_2$	5.37	5.50	−0.06	4.51
$H_4AlAsH_3^+ \rightarrow H_2AlAsH_3^+ + H_2$	4.38	5.02	−2.25	3.40
$H_4AlOH_2^+ \rightarrow H_2AlOH_2^+ + H_2$	4.45	4.48	0.59	3.61
$H_4AlSH_2^+ \rightarrow H_2AlSH_2^+ + H_2$	4.59	5.09	−0.89	3.48
$H_4AlSeH_2^+ \rightarrow H_2AlSeH_2^+ + H_2$	4.25	4.82	−1.33	3.32

[a] At the QCISD(T)/6-311++G(d,p)//MP2(full)/6-31G(d) + ZPE level.

TABLE 5: Entropies (298 K, 1 atm, Ideal Gas) in cal/(mol K) and Thermal Corrections to the Internal Energy in kcal/mol

molecule	entropy	thermal	molecule	entropy	thermal
$H_4AlNH_3^+$	82.09	4.84	$H_2AlNH_3^+$	69.40	2.92
$H_4AlPH_3^+$	85.45	5.12	$H_2AlPH_3^+$	73.68	3.27
$H_4AlAsH_3^+$	83.33	4.70	$H_2AlAsH_3^+$	77.58	3.39
$H_4AlOH_2^+$	79.48	4.72	$H_2AlOH_2^+$	62.53	2.64
$H_4AlSH_2^+$	77.29	4.38	$H_2AlSH_2^+$	67.19	2.93
$H_4AlSeH_2^+$	79.90	4.40	$H_2AlSeH_2^+$	70.42	3.01
H_2	31.06	1.48			

Protonation of H_3AlXH_3 to form $H_4AlXH_3^+$ (X = N, P, and As) are calculated to be highly exothermic by 208.26, 203.63, and 202.64 kcal/mol, respectively (Table 3). Nevertheless, by protonation of the corresponding neutral complexes, the complexation energies increase. Indeed, the protonation stabilizes the complexes by ∼31, ∼27, and ∼26 kcal/mol for H_3AlNH_3, H_3AlPH_3, and H_3AlAsH_3 complexes, respectively. The charge-

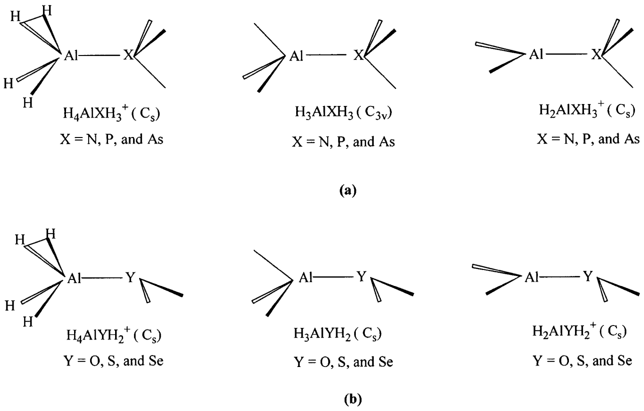
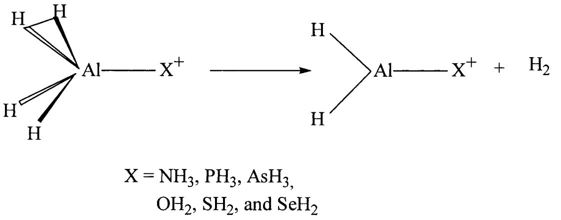


Figure 1. Definition of the geometrical parameters of (a) $H_4AlXH_3^+$, H_3AlXH_3, and $H_2AlXH_2^+$ (X = N, P, and As) and of (b) $H_4AlYH_2^+$, H_3AlYH_2, and $H_2AlYH_2^+$ (Y = O, S, and Se) complexes.

SCHEME 1



transfer varies in the even feel as the complexation energies (Table 3).

On the other hand, structure of $H_4AlXH_3^+$ (X = N, P, and As) can be viewed as a weak complex between $H_2AlXH_3^+$ and molecular H_2. Thus, the dissociation of $H_4AlXH_3^+$ into $H_2AlXH_3^+$ and molecular H_2 (Scheme 1) are endothermic by about 5 kcal/mol (Table 4). The same trend is observed at the QCISD(T)/6-311++G(d,p)//MP2(full)/6-31G(d) + ZPE level. At room temperature (298 K) the dissociation reactions are slightly exothermic (Table 4). In comparison, dissociation of AlH_5 into AlH_3 and H_2 is indicated to be endothermic by 2.9 kcal/mol.[36] The same trend has been reported for the dissociation of H_4BX^+ (X = NH_3, PH_3, OH_2, SH_2, and CO) into H_2BX^+ and molecular H_2.[29]

Complexation of YH_2 (Y = O, S, and Se) with AlH_4^+ leads to C_s symmetry monocation $H_4AlYH_2^+$ which was calculated to be a stable structure at the G2 level of theory. The C_s symmetry structure also contains a five-coordinate aluminum atom with a three-center two-electron (3c-2e) bond (Figure 1). The Al−Y bond length of $H_4AlYH_2^+$ (Y = O, S, and Se) are 1.916, 2.414, and 2.523 Å, 0.135, 0.141, and 0.119 Å shorter than found in H_3AlOH_2, H_3AlSH_2, and H_3AlSeH_2 respectively, at the same MP2(full)/6-31G(d) level of theory which indicate stronger Al−Y bonding in $H_4AlYH_2^+$ than that in H_3AlYH_2. Indeed, the complexation energies $AlH_4^+ + YH_2$ (X = O, S, and Se) are −46.82, −37.76, and −34.97 kcal/mol for $H_4AlOH_2^+$, $H_4AlSH_2^+$, and $H_4AlSeH_2^+$, protonated complexes, respectively, while they are only −16.71, −10.66, and −9.74 kcal/mol for H_3AlOH_2 H_3AlSH_2, and H_3AlSeH_2, nonprotonated complexes, respectively. The complexation energy decreases for each group when descending in the corresponding periodic table column, from oxygen to selenium.

The NBO-MP2(full)/6-31G(d) analysis (Table 3) show that there is no correlation between charge transfer and the G2 complexation energy, as is the case for the protonated $H_4AlXH_3^+$ complexes. For the most stable protonated complex $H_4AlOH_2^+$, the charge transferred is 0.15*e*, while for the less stable complex $H_4AlSeH_2^+$, this transferred charge is 0.34*e*. We note also the same trend for the non protonated complexes. Nevertheless, we notice that the increase of the transferred charge contributes to the stability of $H_4AlYH_2^+$ complexes compared with parents H_3AlYH_2, respectively.

Protonation of H_3AlYH_2 complexes, and also H_3AlXH_3 complexes, to form $H_4AlYH_2^+$ (Y = O, S, and Se) complexes are also calculated to be highly exothermic by 206.48, 200.46, and 201.60 kcal/mol, respectively (Table 3). Upon protonation, the complexation energy and the charge transfer increase. Indeed, the protonation stabilizes the complex by ~30, ~24, and ~25 kcal/mol for H_3AlOH_2, H_3AlSH_2, and H_3AlSeH_2 complexes, respectively.

On the other hand, the structure of $H_4AlYH_2^+$ (Y = O, S, and Se) can also be viewed as a weak complex between $H_2AlYH_2^+$ and H_2. Thus, the dissociation of $H_4AlYH_2^+$ complexes into $H_2AlYH_2^+$ and molecular H_2 (Scheme 1) are slightly endothermic by about 5 kcal/mol (Table 4). At room temperature (298 K) the dissociation reactions are slightly exothermic (Table 4). The same trend is observed for $H_4AlXH_3^+$ complexes.

Let us now examine the evolution of the ∠H−Y−Al angle (Figure 1) along the $H_4AlYH_2^+$ (Y = O, S, and Se) complexation series. This angle decreases on going from $H_4AlOH_2^+$ to $H_4AlSeH_2^+$ (Table 2), respectively. The same evolution has been recently observed and discussed in H_3AlX (X = OH_2, SH_2, and SeH_2) compounds.[26] We have shown that this evolution can be explained by examining the donor fragment orbitals energetic placement in going from the OH_2 ligand to the SeH_2 one. This can rationalize the evolution of the ∠H−Y−Al angle observed in the $H_4AlYH_2^+$ complexes.

4. Conclusion

Complexes of AlH_4^+ with XH_3 (X = N, P, and As) and YH_2 (Y = O, S, and Se) were found to have C_s symmetry with a 3c-2e bond. The formations of the cations $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) were calculated to be exothermic by 33−58 kcal/mol, and the cations themselves were found to be more stable than their nonprotonated parents at the G2 level of theory. The G2 energetic results show that the stability of the protonated alane−Lewis complexes decreases when descending in the corresponding periodic table column, from nitrogen (or oxygen) to arsenic (or selenium) atoms. The G2 calculated protonation energies of $H_3AlXH_3(YH_2)$ to form $H_4AlXH_3(YH_2)^+$ were found to be highly exothermic. The possible dissociation of the cations $H_4AlXH_3(YH_2)^+$ into $H_2AlXH_3(YH_2)^+$ and molecular H_2 are calculated to be endothermic by ~5 kcal/mol. These observations indicate that $H_4AlXH_3^+$ and $H_4AlYH_2^+$ complexes, if stable toward transfer of a proton to X and Y followed by loss of XH_4^+/YH_3^+, should be experimentally observable in the gas phase.

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