Journal of Fluorine Chemistry 130 (2009) 557–561

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Protonated MF_3 (M = N–Bi): Structure, stability, and thermochemistry of the $H–MF_3^+$ and $HF–MF_2^+$ isomers

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ARTICLE INFO

Article history:
Received 10 December 2008
Received in revised form 23 March 2009
Accepted 24 March 2009
Available online 2 April 2009

Keywords:
Gas-phase protonation
Group XV fluorides
Structure and stability
Theoretical calculations
Thermochemistry

ABSTRACT

The structure, stability, and thermochemistry of the $H(MF_3)^+$ isomers (M = N–Bi) have been investigated by MP2 and coupled cluster calculations. All the $HF–MF_2^+$ revealed weakly bound ion–dipole complexes between MF_2^+ and HF. For M = N, As, Sb, and Bi they are more stable than the $H–MF_3^+$ covalent structures (free energy differences) by 6.3, 14.3, 32.1, and 73.5 kcal mol^{-1}, respectively. $H–PF_3^+$ is instead more stable than $HF–PF_2^+$ by 21.8 kcal mol^{-1}. The proton affinities (PAs) of MF_3 at the M atom range from 91.9 kcal mol^{-1} (M = Bi) to 156.5 kcal mol^{-1} (M = P), and follow the irregular periodic trend $BiF_3 < SbF_3 < AsF_3 < NF_3 < PF_3$. The PAs at the F atom range instead from 131.9 kcal mol^{-1} (M = P) to 164.9 kcal mol^{-1} (M = Bi), and increase in the more regular order $PF_3 \approx NF_3 < AsF_3 < SbF_3 < BiF_3$. This trend parallels the fluoride-ion affinities of the MF_2^+ cations. For protonated NF_3 and PF_3, the calculations are in good agreement with the available experimental results. As for protonated AsF_3, they support the formation of $HF–AsF_2^+$ rather than the previously proposed $H–AsF_3^+$. The calculations indicate also that the still elusive $H(SbF_3)^+$ and $H(BiF_3)^+$ should be viable species in the gas phase, exothermically obtainable by various protonating agents.

1. Introduction

The group XV fluorides MF_3 (M = N–Bi) are of both fundamental and applied interest. Most of these compounds are in fact extensively used in the electronic industry to perform etching and cleaning processes [1], to achieve the doping of semiconductors [2], and to deposit amorphous fluorinated materials [3]. All the MF_3 (M = N–Bi) have non-planar structures of C_{3v} symmetry and their bonding, properties, and reactivity have been extensively investigated, both experimentally and theoretically [4–8]. In this paper, we focus on the still only partially explored behaviour of MF_3 as Brønsted bases. Protonated NF_3, not attainable under "magic acid" conditions [9], was observed so far under mass spectrometric conditions [10]. The proton affinity (PA) of NF_3, i.e. the minus enthalpy change of the reaction $H^+ + NF_3 \rightarrow H(NF_3)^+$, was subsequently measured by high-pressure mass spectrometry [11], and is currently compiled as 135.9 kcal mol^{-1} [12]. Based on various experimental and theoretical studies [13–17], this value refers to the fluorine-protonated isomer $HF–NF_2^+$, a weakly bound ion–dipole complex between NF_2^+ and HF structurally distinguishable from the less stable $H–NF_3^+$ [14]. According to various ab initio calculations, the two isomers are separated by 2–6 kcal mol^{-1} [13–17]. Protonated PF_3 was observed so far in the gas phase [18] and the PA of PF_3, measured by different techniques [18,19], is currently compiled as 166.2 kcal mol^{-1} [12]. The structure of the gaseous $H(PF_3)^+$ has never been explored by experimental or theoretical methods, but the observed species has been invariably assigned as the trifluorophosphonium ion $H–PF_3^+$. Consistently, this cation has been recently isolated in the solid salt $H–PF_3^+SbF_6^-$ [20], and structurally characterized by spectroscopic methods and ab initio calculations. Protonated PF_3 was also observed so far in solution under "magic acid" conditions and again assigned as $H–PF_3^+$ by NMR spectroscopy [21]. Gaseous protonated AsF_3 was obtained so far under mass spectrometric conditions [22], and assumed to be the trifluoroarsonium $H–AsF_3^+$. The measured PA of AsF_3, 152.2 kcal mol^{-1} [12], resulted in between NF_3 and PF_3, and this reversed trend was explained in terms of the different electronegativity of M (M = N, P, As), and invoking a different participation of d orbitals in the formation of $H–MF_3^+$. In the same study, it was also observed that $H(AsF_3)^+$ reacts with ligands L such as CO, CO_2, CH_3F, and AsF_3 itself, so to give the displacement of HF and the formation of AsF_2^+–(L). Interestingly, this behaviour closely resembles protonated NF_3, structurally assigned as $HF–NF_2^+$, which undergoes ligand-displacement reactions [13,15] strictly analogue to $H(AsF_3)^+$. Therefore, although mechanisms can be proposed which explain the occurrence of efficient ligand-displacements from $H–AsF_3^+$ [22], a plausible alternative explanation is that at least the reactive form of the gaseous $H(AsF_3)^+$ is indeed the fluorine-protonated structure

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doi:10.1016/j.jfluchem.2009.03.008

HF–AsF$_2^+$. To date, no theoretical calculations have been reported on the structure and stability of the H(AsF$_3$)$^+$ isomers. Interestingly, with the only exception of F$_3$As–Au$^+$SbF$_6^-$ [23], in its metal complexes AsF$_3$ coordinates to the cation typically by its fluorine atom(s) [24]. Finally, neither experimental nor theoretical information is available on protonated SbF$_3$ and BiF$_3$. We therefore decided to undertake a theoretical investigation, at an uniform and accurate level of theory, on the structure, stability, and thermochemistry of the H(MF$_3$)$^+$ isomers (M = N–Bi). The obtained results will be discussed in the present article.

2. Computational details

The calculations were performed with the Gaussian 03 [25] program using the Dunning's correlation consistent double- and triple-zeta basis sets augmented with diffuse functions for the H, N, F, and P atoms [26], and the Los Alamos ECP plus DZ basis set (LANL2DZ) [27] for the As, Sb, and Bi atoms. These basis sets will be denoted here as aug-cc-pVnZ and aug-cc-pVnZ/LANL2DZ, respectively (n = D, T). The geometries of MF$_3$ and of the H(MF$_3$)$^+$ isomers (M = N–Bi) were optimized at the second-order Møller–Plesset level of theory with inclusion of the inner electrons, MP2(full) [28], using the aug-cc-pVDZ (M = N, P) and aug-cc-pVDZ/LANL2DZ basis sets (M = As, Sb, Bi), and the obtained species were unambiguously characterized as energy minima by harmonic frequencies calculations. The total energies were subsequently refined by single-point calculations at the coupled cluster level of theory (full electrons), including the contribution from single and double substitutions and an estimate of connected triples, CCSD(T,full) [29], using the aug-cc-pVTZ and the aug-cc-pVTZ/LANL2DZ basis sets. The proton affinity (PA) and the gas-phase basicity (GB) of MF$_3$, i.e. the minus enthalpy ($-\Delta H$) and the minus free energy ($-\Delta G$) changes at T = 298.15 K and P = 1 atm of the reaction

$$\mathrm{H^+ + MF_3 \rightarrow H(MF_3)^+}$$

were calculated by correcting the coupled cluster electronic energies so to include the zero-point vibrational energies (ZPE), the vibrational contribution to the thermal correction (TC), and the total entropies S. These terms were obtained by standard statistical mechanics formulas [30] using the MP2(full)/aug-cc-pVDZ and MP2(full)/aug-cc-pVDZ/LANL2DZ unscaled frequencies and moments of inertia. The overall TC term was finally obtained by adding the translational (3/2 RT) and rotational (RT or 3/2 RT) contributions at 298.15 K. Our thermochemical data have been corrected for the basis set superposition error (BSSE) using the method by Boys and Bernardi [31]. The MP2(full)/aug-cc-pVDZ and MP2(full)/aug-cc-pVDZ/LANL2DZ atomic charges were calculated by Natural Bond Orbital (NBO) analysis [32] at 0 K of the wave function.

3. Results and discussion

The MP2 optimized geometries of the MF$_3$ molecules and of their M- and F-protonated isomers, henceforth indicated as **1a**–**1e** and **2a**–**2e**, respectively, are shown in Fig. 1. For comparative purposes, we included also the experimental gas-phase structures of MF$_3$ [8,33,34], and the crystal structure of H–PF$_3^+$ (**1b**) [20]. The absolute and relative energies of our investigated species and their NBO total charges are listed in Tables 1 and 2. Their CCSD/aug-cc-pVDZ/LANL2DZ T1 diagnostics [35] resulted invariably around the recommended threshold of 0.02.

All the MF$_3$ molecules possess non-planar structures of C_{3v} symmetry [8,33,34]. Passing from NF$_3$ to BiF$_3$, the experimental M–F bond length increases from 1.367 to 1.979 Å and the F–M–F bond angle decreases from NF$_3$ (101.9°) to SbF$_3$ (94.9°), but slightly increases up to 96.1° in BiF$_3$. From Fig. 1, our MP2 calculations fully reproduce these trends and furnish also absolute bond lengths and bond angles which are in good agreement with the experimental values. We note in particular single largest deviations of 0.057 Å and 0.7° in the predicted geometry of PF$_3$ (similar differences were also obtained between the computed and the experimental parameters of H–PF$_3^+$). We therefore expect that the MP2 level of theory is adequate to predict the geometries of the H–MF$_3^+$ and HF–MF$_2^+$ isomers. Consistently, the geometry optimization of the test cases PF$_3$, **1b**, and **2b** performed at the CCSD(T)/aug-cc-pVDZ

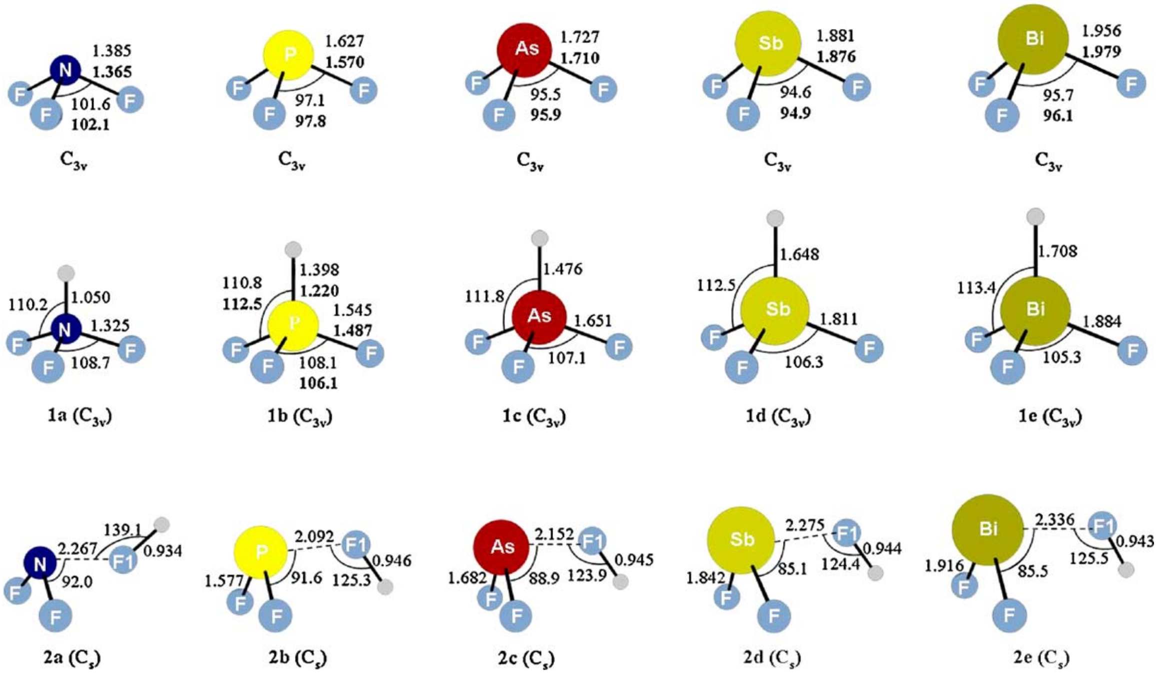

Fig. 1. MP2(full)/aug-cc-pVDZ and MP2(full)/aug-cc-pVDZ/LANL2DZ optimized geometries (Å and °) of MF$_3$, H–MF$_3^+$, and HF–MF$_2^+$ (M = N–Bi). Bold values are experimental data.

Table 1

Total energies (atomic units), zero-point energies (ZPE, atomic units), thermal corrections (TC, atomic units), total entropies (S, cal mol^{-1} K^{-1}), and relative energies (kcal mol^{-1}) of MF_3, $H–MF_3^+$, $HF–MF_2^+$ (see Fig. 1), MF_2^+ and HF, calculated with the aug-cc-pVTZ (M = N, P) and aug-cc-pVTZ/LANL2DZ (M = As, Sb, Bi) basis sets.

	CCSD(T,full)[a]	ZPE[b]	TC[c]	S[d]	ΔH (298.15 K)	ΔG (298.15 K)
NF_3	−353.77164	0.01006	0.00359	62.4		
1a	−353.99975	0.02525	0.00347	62.1	0.0	0.0
2a	−353.99980	0.01896	0.00577	75.0	−2.5	−6.4
PF_3	−640.34560	0.00814	0.00413	66.0		
1b	−640.60873	0.01981	0.00410	65.9	0.0	0.0
2b	−640.56778	0.01682	0.00577	76.4	24.9	21.7
AsF_3	−305.43619	0.00680	0.00447	69.0		
1c	−305.66131	0.01696	0.00453	69.2	0.0	0.0
2c	−305.67987	0.01584	0.00596	78.5	−11.5	−14.2
SbF_3	−304.74611	0.00595	0.00481	72.1		
1d	−304.95829	0.01451	0.00500	72.6	0.0	0.0
2d	−305.00726	0.01519	0.00619	81.0	−29.6	−32.1
BiF_3	−304.77099	0.00541	0.00504	74.7		
1e	−304.93158	0.01301	0.00532	75.5	0.0	0.0
2e	−305.04735	0.01474	0.00642	84.1	−70.9	−73.5
NF_2^+	−253.61187	0.00774	0.00295	57.4		
PF_2^+	−540.16981	0.00535	0.00325	61.2		
AsF_2^+	−205.27931	0.00443	0.00339	64.0		
SbF_2^+	−204.60584	0.00388	0.00354	66.3		
BiF_2^+	−204.64598	0.00358	0.00363	68.4		
HF	−100.36358	0.00930	0.00236	41.5		
H^+			0.00143	26.0		

[a] At the MP2(full)/aug-cc-pVDZ (M = N, P) and MP2(full)/aug-cc-pVDZ/LANL2DZ (M = As, Sb, Bi) optimized geometries.

[b] Based on unscaled MP2(full)/aug-cc-pVDZ (M = N, P) and MP2(full)/aug-cc-pVDZ/LANL2DZ (M = As, Sb, Bi) harmonic frequencies.

[c] At 298.15 K, based on unscaled MP2(full)/aug-cc-pVDZ (M = N, P) and MP2(full)/aug-cc-pVDZ/LANL2DZ (M = As, Sb, Bi) harmonic frequencies.

[d] At 298.15 K, based on unscaled MP2(full)/aug-cc-pVDZ (M = N, P) and MP2(full)/aug-cc-pVDZ/LANL2DZ (M = As, Sb, Bi) harmonic frequencies and moments of inertia.

Table 2

NBO atomic charges (e) of MF_3, $H–MF_3^+$, $HF–MF_2^+$ (see Fig. 1), MF_2^+ and HF, calculated at the MP2(full)/aug-cc-pVTZ (M = N, P) and MP2(full)/aug-cc-pVTZ/LANL2DZ (M = As, Sb, Bi) level of theory (see Fig. 1).

	q (M)	q (F)	q (F1)	q (H)
NF_3	0.657	−0.219		
1a	0.742	−0.078		0.492
2a	0.885	0.036	−0.572	0.615
PF_3	1.785	−0.595		
1b	2.428	−0.484		0.024
2b	1.956	−0.536	−0.522	0.638
AsF_3	2.013	−0.671		
1c	2.718	−0.559		−0.041
2c	2.165	−0.625	−0.553	0.638
SbF_3	2.220	−0.740		
1d	3.051	−0.632		−0.155
2d	2.360	−0.710	−0.579	0.639
BiF_3	2.238	−0.746		
1e	2.891	−0.605		−0.076
2e	2.371	−0.712	−0.584	0.637
NF_2^+	0.890	0.055		
PF_2^+	2.008	−0.504		
AsF_2^+	2.190	−0.595		
SbF_2^+	2.378	−0.689		
BiF_2^+	2.384	−0.692		
HF	0.560	−0.560		

level of theory furnished values nearly identical to the MP2 (PF_3: 1.626 Å/96.8°; **1b**: 1.401 Å/1.545 Å/108.0°/110.9°; **2b**: 0.944 Å/2.099 Å/1.577 Å/125.8°/91.1°). We note also from Table 2 that, according with the qualitatively expected trend, the ionicity of the M–F bond, roughly measured by the charge separation between the M and F atoms, appreciably increases from NF_3 to BiF_3.

Similar to the neutral MF_3, all the $H–MF_3^+$ isomers **1a**–**1e** are predicted to be covalent structures of C_{3v} symmetry. The M–H bond distances regularly increase in the series and are typical of covalent bonds [34]. The M–F bond distances increase also from 1.325 Å (**1a**) up to 1.884 Å (**1e**), and the F–M–F bond angles range between ca. 105° (**1e**) and ca. 109° (**1a**). Therefore, passing from MF_3 to $H–MF_3^+$, we note two clearly appreciable structural effects, namely a shortening of the M–F bond distance by ca. 0.06–0.08 Å and a widening of the F–M–F bond angle by up to ca. 12° (M = Sb). In addition, the negative charge of the F atoms of any $H–MF_3^+$ is lower than the corresponding MF_3 by ca. 0.1 e, and the positive charge of the (H–M)—moiety of $H–MF_3^+$ is larger than the M atom of MF_3 by ca. 0.6 e. Overall, this suggests that the formal attachment of H^+ to the M atom of MF_3 enhances back donation from the surrounding fluorines and reinforces the degree of the M–F interaction. Consistently, we found that, passing from MF_3 to $H–MF_3^+$, the frequencies of the M–F stretching modes increase by ca. 60–80 cm^{-1} (A_1 symmetry) and ca. 120–260 cm^{-1} (E symmetry). We also note from Fig. 1 that the H–M–F bond angle of any isomer **1a**–**1e** is larger than the corresponding F–M–F bond angle. Therefore, as noted previously for the $H–PF_3^+$ isomer **1b** [20], in the view of the VSEPR model, the H atom of any $H–MF_3^+$ appears a slightly larger ligand than the F atom.

The F-protonated isomers **2a**–**2e** share typical structural motifs, namely a strongly elongated $HF–MF_2^+$ bond, whose distance is predicted between 2.092 Å (**2b**) and 2.336 Å (**2e**), a nearly unitary charge on the $–MF_2^+$ moiety, and dissociation enthalpies into MF_2^+ and HF which range from ca. 13 kcal mol^{-1} (**2a**) to ca. 18–21 kcal mol^{-1} (**2b**–**2e**). Therefore, similar to the previously investigated $HF–NF_2^+$ isomer **1a** [13–17], all the F-protonated isomers $HF–MF_2^+$ (M = P–Bi) are best viewed as ion–dipole complexes between the MF_2^+ cation and the HF molecule. With the only exception of the $HF–PF_2^+$ isomer **2b**, which is less stable than $H–PF_3^+$ by ca. 22 kcal mol^{-1} (free energy difference), any $HF–MF_2^+$ results more stable than the corresponding $H–MF_3^+$. As detailed in Table 1, the computed ΔG are 6.3 kcal mol^{-1} (M = N), 14.3 kcal mol^{-1} (M = As), 32.1 kcal mol^{-1} (M = Sb), and 73.5 kcal mol^{-1} (M = Bi). We also note from Fig. 1 that isomer **2a** has a conformation different from **2b** to **2e**. The isomer of **2a** structurally analogue to **2b**–**2e** was in fact characterized as a first-order saddle point.

The stability and thermochemistry of BiF_3 and of ions **1e** and **2e** could be in principle affected by spin–orbit (SO) coupling. The singlet–triplet energy gap of these species resulted however larger than 3–4 eV, thus suggesting that the SO term should not appreciably affect their predicted properties. Interestingly, a recent investigation revealed that the SO term has not an appreciable influence on the structure and the spectroscopic properties of BiH_3 [36].

The PA and the GB of the MF_3 molecules, computed at both the M (formation of isomers **1a**–**1e**) and the F site (formation of isomers **2a**–**2e**), are listed in Table 3 together with the available experimental data [12].

The theoretical PAs of NF_3 at the N and the F atom differ by 3.4 kcal mol^{-1} and result as 132.1 and 135.5 kcal mol^{-1}, respectively. Within the accuracy of our calculations (estimated as nearly 4 kcal mol^{-1}), both these values are compatible with the experimental PA of NF_3, 135.9 kcal mol^{-1}. Even though the experimental GB of NF_3, 128.7 kcal mol^{-1}, is quite close to the value predicted for the F-protonation, it is however also not inconsistent, within combined uncertainities, with the formation of the N-protonated isomer. Therefore, in line with all the previous studies [13–17], we confirm here that, under thermodynamically controlled conditions, the gas-phase protonation of NF_3 leads to a mixture of the nearly degenerate isomers **1a** and **1b**. The theoretical PA of PF_3 amounts to 156.5 kcal mol^{-1} for P-protonation and 131.9 kcal mol^{-1} for

Table 3
Theoretical and experimental proton affinities (PA) and gas-phase basicities (GB) of MF_3 (M = N–Bi) (kcal mol^{-1}).

	PA (theory)	PA (exp.)[a]	GB (theory)	GB (exp.)[a]
NF_3(N)	132.1[b] 137.6[c] 131.8[d] 132.8[e] 141.8[f]		124.3[b]	
NF_3(F)	135.5[b] 139.8[c] 138.2[d] 134.8[e] 146.5[f] 139.6[g]	135.9	130.5[b]	128.7
PF_3(P)	156.5[b]	166.2	148.4[b]	158.4
PF_3(F)	131.9[b]		127.2[b]	
AsF_3(As)	128.7[b]		121.0[b]	
AsF_3(F)	144.4[b]	152.3	139.5[b]	144.4
SbF_3(Sb)	122.4[b]		114.8[b]	
SbF_3(F)	155.3[b]		150.2[b]	
BiF_3(Bi)	91.9[b]		84.4[b]	
BiF_3(F)	164.9[b]		159.9[b]	

[a] Experimental value from Ref. [12].
[b] Present work.
[c] At the HF/6-31G(d,p) level of theory (Ref. [13]).
[d] At the G1 level of theory (Ref. [14]).
[e] At the G2MS level of theory (Ref. [16]).
[f] At the QCISD/6-311+G(2d,2p) level of theory (Ref. [17]).
[g] At the G2+ level of theory (Ref. [15]).

F-protonation. Compared with the experimental value of 166.2 kcal mol^{-1}, we assign the experimentally observed $H(PF_3)^+$ as the trifluorophosphonium ion **1b** rather than the significantly less stable **2b**. In fact, a difference of more than 30 kcal mol^{-1} between the experimental and the theoretical PA of PF_3 would mark an unreasonable failing of the coupled cluster method in predicting thermochemical quantities. The $H–PF_3^+$ cation is also the only species observed in the solid state [20] and in solution [21]. As for protonated AsF_3, the theoretical PA and GB at the F atom, 144.4 and 139.5 kcal mol^{-1}, respectively, are close to the experimental values of 152.3 and 144.4 kcal mol^{-1}, respectively. On the other hand, the predicted PA and GB at the As atom, 128.7 and 120.0 kcal mol^{-1}, respectively, are significantly lower than the experimental values. We therefore suggest that the protonated AsF_3 observed so far in the gas phase and assigned as the trifluoroarsonium ion $H–AsF_3^+$ [22] is indeed the $HF–AsF_2^+$ isomer **2c**, more stable than the As-protonated structure **1c** by ca. 14 kcal mol^{-1}. This assignment easily explains the gas-phase reactions observed for $H(AsF_3)^+$ [22], including in particular the efficient displacement of HF by ligands L so to give the formation of AsF_2^+-(L). These processes well accord in fact with a precursor ion–dipole complex $HF–AsF_2^+$. The PA and GB of SbF_3 and BiF_3 have not yet been experimentally measured. Our calculations suggest that these protonated molecules should be viable species, and indicate the F atoms as the by far favoured protonation sites. In addition, based on the predicted PA of 155.3 and 164.9 kcal mol^{-1}, respectively, both protonated SbF_3 and BiF_3 should be exothermically produced by various protonating agents.

The basicities of the M-protonated MF_3 (M = N–Bi) increase in the order $BiF_3 < SbF_3 < AsF_3 < NF_3 < PF_3$. This trend is irregular with respect to the PAs of the group XV hydrides MH_3 ($AsH_3 < PH_3 < NH_3$), but resembles the order of basicity of other group XV compounds such as $M(CH_3)_3$ ($As(CH_3)_3 < N(CH_3)_3 < P(CH_3)_3$) and MPh_3 ($SbPh_3 < AsPh_3 \approx NPh_3 < PPh_3$) [12]. Such variations have been explained [22] in terms of different participation (maximum for the P atom) of surrounding electrons (p, σ or π) to bonding with d orbitals of the M atom in the $H–MR_3^+$ cation. The basicities of the F-protonated MF_3 show instead a nearly regular increase down group XV, i.e. $PF_3 \approx NF_3 < AsF_3 < SbF_3 < BiF_3$. Due to the ion–dipole character of isomers **2a**–**2e**, based on a simple thermochemical cycle, the PA of MF_3 at the F atom, $PA_F(MF_3)$, can be written as follows:

$$PA_F(MF_3) = -FA(MF_2^+) + BDE(HF-MF_2^+) + 371.3 \quad (1)$$

where $FA(MF_2^+)$ is the fluoride ion affinity of MF_2^+, i.e. the minus enthalpy change of the reaction $MF_2^+ + F^- \rightarrow MF_3$, $BDE(HF–MF_2^+)$ is the dissociation enthalpy of $HF–MF_2^+$ into MF_2^+ and HF, and 371.3 is the deprotonation enthalpy of HF [37] (all quantities are expressed in kcal mol^{-1}). From the data reported in Table 1, the BDE of the various $HF–MF_2^+$ (BSSE-corrected values) cover a range of less than 8 kcal mol^{-1} and amount to 13.1 kcal mol^{-1} (M = N), 18.0 kcal mol^{-1} (M = P), 18.9 kcal mol^{-1} (M = As), 20.2 kcal mol^{-1} (M = Sb), and 20.6 kcal mol^{-1} (M = Bi). Therefore, the sizable periodic increase from 131.9 kcal mol^{-1} (M = P) to 164.9 kcal mol^{-1} (M = Bi) of the $PA_F(MF_3)$ essentially reflects a comparable decrease of the defluoruration enthalpies of the MF_3 molecules. Using Eq. (1), the $FA(MF_2^+)$ are predicted as 248.9 kcal mol^{-1} (M = N), 257.4 kcal mol^{-1} (M = P), 245.8 kcal mol^{-1} (M = As), 236.2 kcal mol^{-1} (M = Sb), and 227.0 kcal mol^{-1} (M = Bi). For NF_2^+ and PF_2^+, these estimates favourably compare with the experimental values of 250.5 and 256.8 kcal mol^{-1}, respectively [37]. This suggests that our calculated FA of AsF_2^+, SbF_2^+, and BiF_2^+ should be reasonably accurate estimates of the still experimentally unknown values. Finally, we note that, at least for PF_2^+ and AsF_2^+, their order of FA is opposite to the experimentally established order of the FA of PF_3 and AsF_3 (with formation of PF_4^- and AsF_4^-, respectively [38]).

4. Concluding remarks

The group XV fluorides MF_3 (M = N–Bi) can in principle behave as bifunctional Brønsted bases. Previous experimental and theoretical studies [13–17] indicated that the F atom of NF_3 is more basic than the N atom by ca. 2–6 kcal mol^{-1}. The present calculations revealed that the F atom is also the more basic site of AsF_3, SbF_3, and BiF_3. The free energy difference between the $HF–MF_2^+$ and $H–MF_3^+$ isomers ranges from 14.3 kcal mol^{-1} (M = As) up to 73.5 kcal mol^{-1} (M = Bi). The experimental PA of AsF_3 is also quite close to the computed basicity of its F atom. We therefore suggest that the $H(AsF_3)^+$ ion observed so far in the gas phase [22] and assigned as $H–AsF_3^+$ is indeed the ion–dipole complex $HF–AsF_2^+$. This explains the efficient displacement of HF so to give AsF_2^+–(L) that these ions undergo by reacting with various ligands L [22]. The still elusive $H(SbF_3)^+$ and $H(BiF_3)^+$ should be also viable species in the gas phase, exothermically obtainable by various protonating agents. As for protonated PF_3, the calculations revealed that the gaseous trifluorophosphonium ion $H–PF_3^+$ is more stable than $HF–PF_2^+$ by more than 20 kcal mol^{-1}. This is consistent with the recent isolation of $H–PF_3^+$ in the solid state [20] and with its previous observation in solution [21].

Acknowledgments

The authors thank the Italian Ministero dell' Università e della Ricerca (MiUR) and the Università della Tuscia for financial support through the "Cofinanziamento di Programmi di Ricerca di Rilevante Interesse Nazionale".

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