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Group IIIA metal dihalide ions: identification of a possible new class of associative ionization reactions

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Abstract

Species of the formula XMY^+ (M = B, Al, Ga; X, Y = F, Cl, Br) are investigated via ab initio quantum chemical calculations employing the G2 procedure and other techniques. We report equilibrium geometries, total energies, and enthalpies of formation for these species, as well as ionization energies of the corresponding radicals XMY. A notable feature of the thermochemistry of XMY^+ is that several examples are found where the reaction $M + XY \rightarrow XMY^+ + e$ is exothermic. If it is assumed that insertion of M into the XY bond can proceed without significant activation energy, these reactions would appear to constitute a new class of associative ionization processes. (Int J Mass Spectrom 184 (1999) 191–199) © 1999 Elsevier Science B.V.

Keywords: Associative ionization; Ab initio calculations; Ionization energies; Reaction thermochemistry

1. Introduction

The halogens, especially fluorine, are notable for possessing very low bond strengths in the elemental form while yielding compounds having much larger bond strengths. For example, the insertion of atomic Mg into the F_2 bond

$$Mg + F–F \rightarrow F–Mg–F \quad (1)$$

is exothermic by 872 kJ mol^{-1} according to tabulated enthalpies of formation [1]. While highly exothermic reactions such as (1) are unlikely to occur by pure association per se (if the reactants are only atomic or diatomic) because of the small number of vibrational degrees of freedom available within the collision complex, there very often exist competing bimolecular product channels which, if exothermic, may be of high efficiency. One particular product channel, which will be exothermic if the total increase in bond strength exceeds the ionization energy of the association product, is that of associative ionization:

$$A + B \rightarrow AB^+ + e \quad (2)$$

Instances where reaction (2) is exothermic for ground-state reactants are rare, because the ionization energy of a small molecule typically exceeds the strength of a "normal" ionic or covalent bond. Previous studies have identified the reactions of CH + O [2,3], Zr + O [4,5], Ba + OH [5,6], La + O_2 [7–9], and possibly Ti + O [4,5,10–12] as examples of exothermic associative ionization. All of these processes are characterized by formation of ions possessing highly polar, multiple bonds (treating $BaOH^+$ as protonated BaO), most often featuring also a metal atom as a reactant.

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Reactions of transition metal and rare-earth atoms with O may well form the most "heavily populated" class of associative ionization reactions, being exothermic for perhaps a score of different metal atoms M [13], and several such processes may be of significance as ionization mechanisms within cold, quiescent gas-phase environments such as dense interstellar clouds [3,5,13–16].

In the present work, we explore the possibility that "insertive ionization" processes of the form

$$\mathrm{M} + \mathrm{XY} \rightarrow \mathrm{XMY}^{+} + e \tag{3}$$

(X, Y = F, Cl, Br) may be exothermic due to the formation of strong M–X and M–Y bonds in a species XMY expected to possess a low ionization energy. We have selected M = B, Al, and Ga as the most electropositive elements (of the first, second, and main-group third rows, respectively) possessing three or more valence electrons, since it might be expected that such elements are among the best candidates for exothermicity of reaction (3). We have used the well-characterized G2 theoretical procedure [17,18] to determine the thermochemistry of reaction (3) as well as its various possible competing bimolecular product channels. Reaction (3) has not been previously identified as an example of associative ionization, but appears comparatively amenable to experimental study.

2. Theoretical methods

The G2 (Gaussian-2) procedure is a well-established technique for determining total energies of small compounds of the first- and second-row elements [17,19,20]. More recently, G2 theory has been extended to also encompass the third-row elements Ga to Kr [18]. Standard G2 theory is parameterized as

$$\begin{aligned} E_0(\mathrm{G2}) = {} & E_e(\mathrm{MP4/6\text{-}311{+}G^{**}}) + E_e(\mathrm{MP4/6\text{-}311G}(2df, p)) - 2E_e(\mathrm{MP4/6\text{-}311G^{**}}) \\ & + E_e(\mathrm{QCISD(T)/6\text{-}311G^{**}}) + E_e(\mathrm{MP2/6\text{-}311{+}G}(3df, 2p)) + E_e(\mathrm{MP2/6\text{-}311G^{**}}) \\ & - E_e(\mathrm{MP2/6\text{-}311{+}G^{**}}) - E_e(\mathrm{MP2/6\text{-}311G}(2df, p)) + \mathrm{HLC} + \mathrm{ZPE} \end{aligned} \tag{4}$$

where HLC denotes an empirical higher-level correction dependent upon the number of α and β valence electrons, where ZPE is the zero-point vibrational energy obtained using scaled HF/6-31G* frequencies, and where all single-point calculations (employing MP2(full)/6-31G* optimized geometries) implement the frozen-core (FC) approximation. The G2 procedure effectively emulates a QCISD(T)(fc)/6-311+G(3df,2p) total energy calculation [19] at a fraction of the computational expense of the latter technique, and is generally considered to yield total energies accurate to within ± 8 kJ mol^{-1} [20]. In the present work, we have also performed calculations using other variants of G2, namely G2(ZPE = MP2) [21], used in those cases where large differences were obtained between the HF/6-31G* and MP2/6-31G* optimized geometries, or where optimization at HF/6-31G* was not successful; and G2(thaw), which includes within the correlation space some orbitals normally relegated to the "frozen core" (2s and 2p in aluminium, and 3d in gallium) [22]. As we have previously described in greater detail [23,24], the G2(thaw) procedure is characterized as

$$E_0[\mathrm{G2(thaw)}] = E_0[\mathrm{G2(raw)}] + m\Delta_{\mathrm{M}} \tag{5}$$

where E_0 [G2(raw)] is obtained in a manner entirely analogous to E_0 (G2) described in Eq. (4), except that all constituent single-point calculations include the set of 2s and 2p (Al) or 3d (Ga) orbitals amongst those correlated. Of the other parameters in Eq. (5), m is the number of metal atoms in the species being studied, while Δ_{M} has the values +0.14022 Hartrees for Al [24] and +0.17430 Hartrees for Ga, obtained as

$$\Delta_{\mathrm{M}} = E_0(\mathrm{M})[\mathrm{G2}] - E_0(\mathrm{M})[\mathrm{G2(raw)}] \tag{6}$$

The purpose of Δ_{M} is to calibrate the G2(thaw) values to the same total energy scale used in G2. All

Table 1
Equilibrium geometries, optimized at the MP2(full)/6-31G* level of the linear ions XMY^+

Species	r(M–F)[a]	r(M–Cl)[a]	r(M–Br)[a]
FBF^+	1.239	—	—
$FBCl^+$	1.246	1.602	—
$FBBr^+$	1.249	—	1.758
$ClBCl^+$	—	1.609	—
$ClBBr^+$	—	1.609	1.763
$BrBBr^+$	—	—	1.765
$FAlF^+$	1.606	—	—
$FAlCl^+$	1.609	1.991	—
$FAlBr^+$	1.612	—	2.144
$ClAlCl^+$	—	1.997	—
$ClAlBr^+$	—	1.999	2.153
$BrAlBr^+$	—	—	2.156
$FGaF^+$	1.685	—	—
$FGaCl^+$	1.687	2.046	—
$FGaBr^+$	1.691	—	2.191
$ClGaCl^+$	—	2.054	—
$ClGaBr^+$	—	2.057	2.194
$BrGaBr^+$	—	—	2.200

[a] Bond length, in Ångstroms.

Table 2
Total energies and enthalpies of formation for XMY^+, obtained at the G2 level of theory

Species	ZPE[a]	E_0[b]	$\Delta H^o_{f,0}$[c]	Lit.[d]
FBF^+	8.52	−224.015 62	324.0	315.8 ± 2.5
$FBCl^+$	7.03	−584.014 69	483.7	
$FBBr^+$	6.51	−2696.848 96	548.8	
$ClBCl^+$	5.47	−944.007 96	658.6	665.4 ± 25
$ClBBr^+$	5.08	−3056.840 39	728.6	
$BrBBr^+$	4.56	−5169.672 55	799.2	
$FAlF^+$[e]	4.97	−441.300 86	210.8	87 ± 63
$FAlCl^+$[e]	4.05	−801.301 88	365.4	271 ± 126
$FAlBr^+$[e]	3.74	−2914.140 66	418.6	
$ClAlCl^+$[e]	3.16	−1161.300 54	526.1	475 ± 75
$ClAlBr^+$[e]	2.94	−3274.138 13	582.5	
$BrAlBr^+$[e]	2.45	−5386.975 46	639.6	
$FGaF^+$	4.22	−2122.388 86	732.0	
$FGaCl^+$	3.40	−2482.471 52	672.3	
$FGaBr^+$	3.05[f]	−4595.316 05[g]	710.5	
$ClGaCl^+$	2.60[f]	−2842.554 42[g]	611.9	
$ClGaBr^+$	2.27[f]	−4955.398 76[g]	650.5	
$BrGaBr^+$	1.87	−7068.242 70	690.3	

[a] Zero-point energy (ZPE), in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}) obtained as the corrected value from the HF/6-31G* geometry unless otherwise indicated.
[b] Total energy, in Hartrees, including ZPE.
[c] 0 Kelvin enthalpy of formation, in kJ mol^{-1}.
[d] Experimental (0 K) enthalpy of formation where available, taken from the JANAF thermochemical tabulation [26].
[e] Previously reported in [27].
[f] ZPE obtained at the MP2(full)/6-31G* level of theory, and corrected by a factor of 0.9427.
[g] G2(ZPE = MP2) value [21].

calculations were performed using the GAUSSIAN 94 software package [25].

3. Results and discussion

Optimized geometries for XMY^+ species, obtained at the MP2(full)/6-31G* level of theory, are summarized in Table 1. Total energies and 0 K enthalpies of formation for these species, obtained using the standard G2 procedure, are given in Table 2. Results of G2(thaw) calculations upon various XMY^+ species are shown in Table 3.

Some trends common to the three "families" of XBY^+, $XAlY^+$, and $XGaY^+$ are apparent. First, all species are found to possess linear geometries and the electronic states $^1\Sigma$ ($C_{\infty v}$) or $^1\Sigma_g$ ($D_{\infty h}$). Second, there is a consistent lengthening of the M–X bond as Y is changed from fluorine to chlorine to bromine: this can be rationalized as indicating a higher contribution from a "fully ionic" structure $[X^- \cdots M^{3+} \cdots Y^-]$, and a lower contribution from a "fully covalent" structure $[X \cdots M^+ \cdots Y]$, when Y = F than when Y = Cl or Br, and the Mulliken charges found for individual atoms within the various structures are consistent with such a description. Third, when the best values for $E_0(XMY^+)$ are used, we find that the enthalpy of reaction (3) is lowest (most negative, or least positive) for XY = F_2, and highest (invariably positive) for XY = Br_2.

We shall discuss separately, below, further details of our results for boron-, aluminium-, and gallium-containing species.

3.1. XBY^+

Good agreement is obtained between our G2 results and the literature values of $\Delta H^o_f(BF_2^+)$ and $\Delta H^o_f(BC1_2^+)$, the only boron dihalide cations to have been subjected to previous experimental study [26].

Table 3
Total energies and enthalpies of formation for selected XMY^+ species obtained using the G2(thaw) procedure

Species	E_0[a] (Hartree)	$\Delta H^o_{f,0}$[b] (kJ mol^{-1})	ΔE_0(thaw)[c] (mHartree)
$FAlF^+$	−441.297 34	220.0	+3.52
$FAlCl^+$	−801.299 27	372.2	−6.82
$FGaF^+$	−2122.508 63	417.6	−119.77
$FGaCl^+$	−2482.535 61	504.0	−64.09
$FGaBr^+$	−4595.380 90	540.2	−64.85
$ClGaCl^+$	−2842.557 22	604.5	−2.80
$ClGaBr^+$	−4955.400 94	644.8	−2.18
$BrGaBr^+$	−7068.244 12	686.6	−1.42

[a] Total energy including ZPE obtained using the G2(thaw) technique.
[b] Enthalpy of formation at 0 K, with an estimated uncertainty of ±10 kJ mol^{-1}.
[c] Change in E_0(G2) due to inclusion of (Al 2*s* and 2*p*; or Ga 3*d*) inner electron correlation.

Our calculations show that the boron/halogen B–X bond strengths in these ions are only weakly dependent on the nature of the other halogen Y. If we define the deviation from bond additivity, δ[BA], as

$$\delta[\mathrm{BA}(\mathrm{XMY}^+)] = \Delta H^o_{f,0}(\mathrm{XMY}^+) - [\Delta H^o_{f,0}(\mathrm{XMX}^+) + \Delta H^o_{f,0}(\mathrm{YMY}^+)]/2 \quad (7)$$

then we obtain δ[BA] values for $FBCl^+$, $FBBr^+$, and $ClBBr^+$, respectively, of −7.6, −12.8, and −0.3 kJ mol^{-1}; that is, the enthalpies of formation of the heterogenous dihalide cations are only marginally below the averages of the corresponding homogeneous dihalide cations. The somewhat larger absolute δ[BA] values for $FBCl^+$ and $FBBr^+$ than for $ClBBr^+$ perhaps indicate that the electron-withdrawing tendency of fluorine in FBF^+ has served to additionally destabilize this species by heightening the effective charge on the boron.

3.2. $XAlY^+$

Experimental determinations of $\Delta H^o_f(XAlY^+)$ have been obtained only for AlF_2^+ and $AlClF^+$, and these are in serious disagreement with the G2 thermochemical parameters obtained in the present study. We have commented elsewhere [27] on the discrepancy: the experimental uncertainties on all of the aluminium dihalide cations and neutrals are very large [26], and we have argued that, since G2 performs very well for all aluminium/halide species of accurately known thermochemistry, it is most likely the experimental values for the aluminium dihalides which are in error. As a check on the reliability of the G2 results, we have also determined G2(thaw) total energies for AlF_2^+ and $AlClF^+$ to ascertain whether any significant inaccuracy results from the implementation of the frozen-core technique on Al in these species. We have previously found that G2 severely overestimates the enthalpies of formation of cations containing both Na and F [23,24]. A comparison of the G2 and G2(thaw) total energies for AlF_2^+ and $AlClF^+$ indicates that there is very little effect arising from inclusion or exclusion of the Al 2*s* and 2*p* orbitals amongst those correlated, which suggests that the G2 total energies are indeed reliable. We can note also that the bond additivity arguments, which hold reasonably well for boron, are adhered to rather more closely for the $XAlY^+$ species (δ[BA] = −3.0, −6.6, and −0.3 kJ mol^{-1}, respectively, for $FAlCl^+$, $FAlBr^+$, and $ClAlBr^+$), consistent with the greater metallic character of aluminium versus boron.

3.3. $XGaY^+$

None of these species appear to have been subjected to previous experimental study, and so they cannot be assessed except on the basis of internal consistency. One computational problem which is evident for these compounds, but not for the analogous B- or Al-containing species, is that the gallium 3*d* orbitals (which are supposedly "core" orbitals, and not to be correlated in the G2 calculations) are higher in energy than the fluorine 2*s* orbitals (which are valence orbitals, requiring correlation) in compounds containing both Ga and F: thus, blind implementation of the G2 procedure (which freezes orbitals from the lowest up) results in an incorrect correlation space being used for these compounds [22,28]. In consequence, the G2 results for $FGaF^+$, $FGaCl^+$, and $FGaBr^+$ reported in Table 2 are expected to be very significantly in error. Much more accurate values

Table 4
Equilibrium geometries, optimized at the MP2(full)/6-31G* level, of the radicals XGaY[a]

Species[a]	r(M–F)[b]	r(M–Cl)[b]	r(M–Br)[b]	∠(XMY)[c]
FGaF	1.751	—	—	116.0
FGaCl	1.751	2.171	—	117.0
FGaBr	1.751	—	2.328	117.2
ClGaCl	—	2.168	—	119.0
ClGaBr	—	2.170	2.325	119.2
BrGaBr	—	—	2.327	119.3

[a] MP2(full)/6-31G* geometries for the analogous B- and Al-containing species have been separately reported in [29] and [27], respectively.
[b] Bond length, in Ångstroms.
[c] Bond angle, in degrees.

should be delivered by the G2(thaw) procedure, which expands the correlation space so that the "mismatch" between Ga and F orbital energies is not a problem: we can see in Table 3 that implementation of G2(thaw) gives much lower, and more believable, enthalpies of formation for $FGaF^+$, $FGaCl^+$, and $FGaBr^+$, while the values delivered by G2 and G2(thaw) for the other three gallium dihalide cations (which do not have any awkward orbital energies) are in very good agreement. Finally, since gallium is less "metallic" than aluminium, it is not surprising to note that the δ[BA] values are somewhat greater in magnitude for Ga (−10.8, −13.8, and −0.6 kJ mol^{-1}, respectively, for $FGaCl^+$, $FGaBr^+$, and $ClGaBr^+$) than for the corresponding aluminium-containing species.

While the data embodied in Tables 2 and 3 are sufficient to determine the thermochemistry of associative ionization (at 0 K) for all of the M/XY systems encompassed in the present study, it is desirable to also have information on the exothermicity of competing channels. We have reported elsewhere the G2 total energies for boron and aluminium dihalide radicals [27,29]; in Tables 4 and 5 we have listed the optimized geometries and G2 total energies, respectively, of gallium-containing compounds connected to the present study. As with the gallium dihalide cations, a paucity of literature values prevents a proper assessment of the G2 thermochemistry of the gallium monohalide or dihalide neutrals: our value of $\Delta H^{o}_{f,0}(GaF) = -242.2$ kJ mol^{-1} is in reasonable accord with the value of −226 kJ mol^{-1} cited by Lias et al. [1]. Note, also, that due to difficulties in defining a standard "frozen core" for neutrals containing both F and Ga [22,24,28], the parameters in Table 5 for GaF, FGaF, FGaCl, and FGaBr are G2(thaw) values.

We can now assess the thermochemistry of the various reactions M + XY, with regard to association

$$M + XY \rightarrow XMY \quad (8)$$

halogen abstraction

$$M + XY \rightarrow MX + Y \quad (9)$$

and associative ionization (3), and our calculated results (obtained at the G2 or G2(thaw) level, as

Table 5
Total energies and enthalpies of formation for GaX and for XGaY, obtained at the G2 level of theory unless otherwise indicated

Species[a]	ZPE[b]	E_0[c]	$\Delta H^{o}_{f,0}$[d]
GaF	1.40	−2023.097 63[e]	−242.2
GaCl		−2383.091 98[f]	−70.1
GaBr	0.54	−4495.929 28	−12.9
FGaF	3.44	−2122.845 62[e]	−467.2
FGaCl	2.69	−2482.848 34[e]	−317.1
FGaBr	2.43	−4595.686 40[e]	−261.9
ClGaCl	1.95	−2842.848 48	−160.2
ClGaBr	1.68	−4955.687 16	−106.6
BrGaBr	1.42	−7068.525 86	−53.1

[a] G2 total energies for the analogous B- and Al-containing species have been separately reported in [29] and [27], respectively.
[b] Zero-point energy, in mHartrees (1 mHartree = 2.6255 kJ mol^{-1}) obtained as the corrected value from the HF/6-31G* geometry unless otherwise indicated.
[c] Total energy, in Hartrees, including ZPE.
[d] 0 K enthalpy of formation, in kJ mol^{-1}.
[e] G2(thaw) value.
[f] Previously reported in [18].

Table 6
Calculated 0 K enthalpies of reaction for processes of the form M + XY → products

Reactants	ΔH^o/kJ mol^{-1} [a]				
	XMY	MF + X	MCl + X	MBr + X	XMY$^+$+e
B + F_2	−1062.2	−603.4	—	—	−235.2
B + FCl	−767.2	−501.3	−259.2	—	−15.7
B + FBr	−693.8	−509.1	—	−176.0	43.3
B + Cl_2	−604.6	—	−279.0	—	97.2
B + ClBr	−547.9	—	−305.3	−214.2	142.6
B + Br_2	−496.1	—	—	−243.4	185.9
Al + F_2	−955.1	−522.9	—	—	−120.6
Al + FCl	−693.3	−420.8	−250.4	—	118.6
Al + FBr	−631.3	−428.6	—	−186.6	141.1
Al + Cl_2	−556.8	—	−272.1	—	190.7
Al + ClBr	−511.6	—	−296.4	−224.9	224.5
Al + Br_2	−471.4	—	—	−254.0	254.2
Ga + F_2[b]	−739.8	−437.5	—	—	144.9
Ga + FCl[b]	−529.9	−335.4	−205.5	—	291.2
Ga + FBr[b]	−480.8	−343.2	—	−154.4	321.3
Ga + Cl_2	−436.9	—	−227.3	—	335.1
Ga + ClBr	−406.0	—	−251.5	−192.7	351.2
Ga + Br_2	−379.9	—	—	−221.8	363.5

[a] Exothermicity at 0 K (obtained at the G2 level of theory unless otherwise indicated) for the indicated product channel.
[b] G2(thaw) values.

appropriate) are given in Table 6. Some very regular trends are apparent in these data. First, the reaction enthalpy for association is lowest when B is the reactant "metal" atom or when F_2 is the reactant dihalogen molecule, and highest when the reactants include Ga or Br_2: nevertheless, this channel is (as expected) always highly exothermic. Second, MF formation is always more exothermic than MCl formation, while MCl is favoured over MBr on energetic grounds; metal halide formation is universally exothermic by at least 150 kJ mol^{-1}. Finally, the ΔH^o values for associative ionization (3) increase uniformly for the sequence of halogens F_2, FCl, FBr, Cl_2, ClBr, and Br_2, and for the sequence of metals B, Al, and Ga. To further assist in the analysis of these trends, we have also listed the calculated ionization energies of XMY radicals (Table 7).

There are only three instances here where associative ionization is calculated to be exothermic: namely, for B + F_2, for B + FCl (marginally), and for Al + F_2. For the case of B + F_2, we have also performed a series of calculations at the B3-LYP/6-311+G* level of theory, the results of which are displayed in Fig. 1. These calculations indicate that insertion of B into the F–F bond occurs without an apparent barrier, and that electron detachment from [BF_2]*, where the collision complex retains all of the internal energy released by B + F_2 association, is energetically accessible as a "vertical" process. We can surmise that, for the example of B + F_2 at least, the associative ionization process appears to lack any activation energy barrier, and can occur in competition with association and with F atom abstraction. Additional support for this

Table 7
Calculated ionization energies of the radicals XMY

Species	IE(XMY)(eV)[a]		
	M = B	M = Al	M = Ga
FMF	8.57	8.65[b]	9.17[c]
FMCl	7.79	8.16[b]	8.51[c]
FMBr	7.64	8.00[b]	8.31[c]
ClMCl	7.25	7.75[b]	8.00
ClMBr	7.16	7.63[b]	7.85
BrMBr	7.07	7.52[b]	7.71

[a] Obtained at the G2 level of theory, unless otherwise indicated.
[b] Previously reported in [27].
[c] G2(thaw) value.

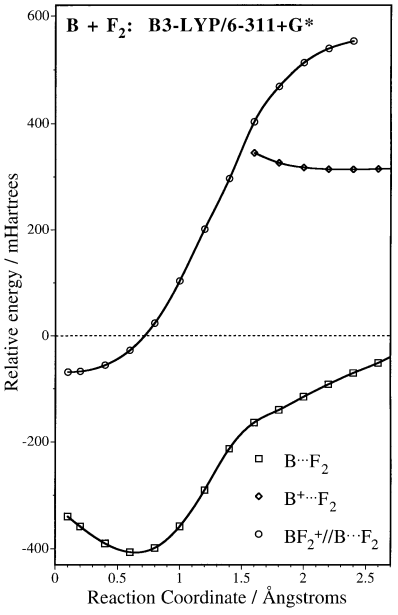

Fig. 1. Potential energy curves obtained for the insertion of B, or B^+, into the F–F bond, obtained at the B3-LYP/6-311+G* level of theory. The reaction coordinate is defined here as the distance between the B atom and the F–F bond midpoint, and the energies are expressed relative to the total energy of $B + F_2$ at infinite separation, at this level of theory: the dashed line indicates which portions of the various potential energy curves are energetically accessible to reactants. Zero-point energy is not included. The curve shown for $BF_2^+//B \cdots F_2$ is for a series of single-point calculations performed using the partially optimized $B \cdots F_2$ geometries, and thus shows the energetic requirements for vertical ionization of the *x* species as a function of the reaction coordinate. Also shown is the curve for association of B^+ with F_2.

notion is obtained from G2 calculations of the total energies for XMY^+ species constrained at the corresponding neutral XMY equilibrium geometry: for these bent configurations of BF_2^+, $BFCl^+$, and AlF_2^+, total energies of −223.943 69, −583.950 13, and 441.263 62 Hartrees lie, respectively, 46.4 kJ mol^{-1} below, 153.8 kJ mol^{-1} above, and 22.8 kJ mol^{-1} below the separated reactants M + XY. These results suggest that both B and Al will have viable vertical associative ionization product channels with F_2, while vertical associative ionization of B with FCl is strongly disfavoured.

It is somewhat surprising to note that boron possesses a greater facility for associative ionization than either Al or Ga, since the ionization energy (IE) of the boron atom (IE = 8.298 eV) is more than 2 eV higher than those of Al (5.986 eV) and Ga (5.99 eV) [1]. If the metal/halogen bond strengths in FMF^+ were identical for all three M atoms (B, Al, and Ga), then reaction (3) would be least favourable for B on energetic grounds and almost equally favoured for Al and Ga: this is clearly not the case. An alternative interpretation of the thermochemical trends involves comparison of the energetics of association and ionization. If we consider associative ionization as a two-step process involving first association (8) followed by ejection of an electron

$$XMY \rightarrow XMY^+ + e \tag{10}$$

then the enthalpy of reaction (3) can be expressed as $\Delta H_8^o + \Delta H_{10}^o$, where ΔH_{10}^o = IE(XMY). The ionization energies of the radicals XMY are all broadly similar, ranging from 7.0 to 9.2 eV; furthermore, the lowest ionization energies are seen for the dibromides and the highest IE values are found for the difluorides. This trend is very much outweighted by the reverse trend in enthalpies of association of M + XY; furthermore, the association enthalpies are much more dependent upon the nature of the metal atom than are the ionization energies. In summary, the metal/halogen bond strength is the main factor influencing the thermochemistry of reaction (3).

The situation observed here, that reaction (3) is most favourable for the first-row element B and least favourable for the third-row element Ga, is much different from the case of transition metal/oxygen atom associative ionization

$$M + O \rightarrow MO^+ + e \tag{11}$$

which, among first-transition-row atoms is exothermic only for Sc and possibly Ti; of second-transition-row atoms, (10) is exothermic by more than 1.5 eV for Y, Zr, and Nb; while almost all of the lanthanides are capable of exothermic associative ionization with O [1,13]. The apparent differences in the exothermicity trends for reactions (3) and (11) probably arise because of differences in the nature of the M–O and M–F bonds: oxygen is more likely than fluorine to confer additional bond strength by back-donation

(favouring a somewhat "covalent" interaction with the charge spread over MO^+), while the extremely high electronegativity of F can act to destabilize FMX^+ to an extent by localizing the positive charge upon the metal atom M.

It would be most interesting to know whether reaction (3) is exothermic also for some reactions of transition-metal atoms: however, the treatment of transition-metal elements by *ab initio* theory is generally a more complicated task than is the calculation of purely main-group compounds, and there are currently no "model chemistry" methods (such as GAUSSIAN-2 [17,18] or the complete basis set (CBS) methods [30,31]) which have been extended to provide highly accurate energies for transition-metal-containing compounds. In consequence, we have not attempted any investigation of reaction (3) for transition-metal atoms, although the limited experimental thermochemistry of metal/fluorine-containing neutrals and ions [1] suggest that the associative ionization reactions of Sc or Y with F_2, for example, might well be exothermic.

In summary, we are able to suggest that the reactions of B with F_2 and FCl, and Al with F_2, are capable of exhibiting exothermic associative ionization. Techniques for generation of gas-phase metal atoms, by laser ablation or other methods, are now fairly well established: in fact, the reaction between atomic boron and X_2 (X = F, Cl, Br, I) has already been studied, but with X_2 embedded in an argon matrix at 12 ± 1 K [32]. Under the conditions imposed on this experimental study, it is not surprising to note that the only primary products observed were the neutral adducts BX_2: we would anticipate that, in the gas phase, the occurrence of biomolecular product channels such as (3) or (9) would be greatly favoured.

4. Conclusions

High-level ab initio calculations indicate that the reactions of B + F_2, B + FCl, and Al + F_2 possess exothermic associative ionization channels: while several examples are known of associative ionization reactions of the forms M + O and M + O_2, there are few examples known of exothermic associative ionization of the type M + F, and (apparently) no previously known examples for M + XY, where XY is a dihalogen. The present study has also provided useful thermochemical data on several metal/halide radicals and ions, particularly those containing gallium which, to date, have not been subjected to experimental study.

A laboratory investigation of the reactions of boron and aluminium atoms (and perhaps also of other atoms, particularly from the transition metals) with halogens, especially with F_2, is strongly urged to determine whether these reactions do indeed possess significant branching ratios for associative ionization.

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