Thermochemistry of Aluminum Halides: A Theoretical Appraisal

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The Gaussian-2 (G2) ab initio procedure has been applied to gas-phase species of the formulas AlX^{n+}, $AlXY^{n+}$, and $AlXYZ^{n+}$ ($n = 0, 1$; X, Y, Z = F, Cl, Br). Existing thermochemical values for several of these species are highly uncertain, and many appear not to have been subjected to any previous study. The G2 results reported herein can be assessed against eight aluminum halides (namely AlF, AlCl, AlF^+, AlF_iCl_{3-i} ($i = 0-3$), and $AlBr_3$) whose enthalpies of formation are known to an accuracy of ±10 kJ mol^{-1} or better: in all cases, very good agreement is found between G2 and the literature values, while the literature values for several other species of uncertain thermochemistry are found to disagree with the G2 results despite large experimental uncertainties. In particular, we urge further experimental examination of the thermochemistry of AlF_2, AlFCl, and $AlCl_2$ and their molecular cations, for which the enthalpies of formation recommended in the JANAF thermochemical tables appear to be systematically too low.

Introduction

The tendency of aluminum to form either monovalent (e.g., AlF, AlCl) or trivalent (e.g., $AlBr_3$, $AlCl_3$) halides can be understood to arise from the necessity for Al 3*s* → 3*p* electron promotion in order to form trivalent, sp^2-hybridized compounds. While the trivalent species are of much greater stability than their univalent analogues in the crystalline state or in solution, species such as AlF become quite stable at high temperatures in the gas phase. Indeed, univalent (but not trivalent) aluminum has been detected in astrophysical environments, as exemplified by the species AlCl and AlF, which have been observed in the hot inner regions of the carbon-rich, circumstellar envelope IRC +10216.[1,2]

While the thermochemistry of the gas-phase species AlX and AlX_3 (X = F, Cl, Br) is quite well-established, such that the enthalpies of formation of these species are known to within ±13 kJ mol^{-1} or better,[3] the same cannot be said for their dissociation or ionization products. Previous experimental investigations concerning $AlX^{\bullet+}$, $AlX_2^{\bullet}$, AlX_2^+, and $AlX_3^{\bullet+}$ have yielded results that are inconclusive or inconsistent with the results of other studies. The inadequacies of current thermochemical values for the radicals or cations are perhaps best exemplified by the values of $\Delta H^\circ_{f,0}(AlCl_2^+) = 475 \pm 75$ kJ mol^{-1}, $\Delta H^\circ_{f,0}(AlClF^+) = 271 \pm 126$ kJ mol^{-1}, and $\Delta H^\circ_{f,0}(AlF_2^+) = 87 \pm 63$ kJ mol^{-1}, as listed in the 1985 JANAF tabulation of recommended thermochemical parameters.[3] The very large uncertainties in these literature values represent the cumulation of the (typically sizable) uncertainties in $\Delta H^\circ_{f,0}(AlXY^{\bullet})$ and in IE($AlXY^{\bullet}$) [X, Y = F, Cl].

Within recent years, substantial advances in the memory capacity and processing speed of computers, as well as the development of several "model" schemes based upon high-level ab initio quantum chemical calculations, have permitted ample demonstration of the general reliability of quantum chemical calculations in the characterization of small molecular species. In particular, the Gaussian-2 (G2) procedure[4] and some of its variants have gained widespread utility as generalized computational methods against which experimental data can usefully be assessed. In the present work, we report the results of a G2 study of aluminum/halide thermochemistry.

Theoretical Methods

The G2 procedure[4] is an ab initio method for the calculation of thermochemical properties of small molecules, molecular ions, and radicals. G2 theory employs a sequence of single-point total energy calculations at various levels of theory, which are used to emulate a total energy calculation at the QCISD(T)/6-311+G(3df,2p) level of theory followed by the incorporation of an additional "higher level correction". Molecular geometries are obtained at two levels of theory: HF/6-31G* (to determine zero-point vibrational energies) and MP2(full)/6-31G* (for use in the single-point total energy calculations).

While the implementation of G2 theory for molecules comprising only first- and second-row atoms is now essentially routine, the extension of G2 to encompass the third-row elements Ga → Br is comparatively recent,[5,6] and some uncertainty exists regarding the inclusion or exclusion of the filled 3d atomic orbitals among those treated for electron correlation.[7] In the present work, we have opted to place the Br 3d orbitals among the "frozen core" of uncorrelated orbitals, in line with the recommendations of the original paper on G2 theory for third-row atoms.[6]

One of the principal aims of G2 theory is to deliver enthalpies of formation that are reliable to within a stated target accuracy of ±2 kcal mol^{-1} (±8.4 kJ mol^{-1}).[4] In fact, while G2 has been shown to provide $\Delta H^\circ_{f,0}$ values to an average deviation from experiment of only ±4.85 kJ mol^{-1} for many small molecules, radicals, and molecular ions containing one or two atoms from the series Li−F and Na−Cl,[4] the deviation becomes significantly greater when three or more "heavy" atoms are present.[8,9] The G2 method is also less accurate for polyfluorinated or polychlorinated compounds than for other species;[9] this latter observation is of some concern for the species studied here, especially since, in the case of fluorinated compounds, the source

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TABLE 1: Equilibrium Geometries for Aluminum/Halide Species, Optimized at the MP2(full)/6-31G* Level[a]

species	r(Al−F)[b]	r(Al−Cl)[b]	r(Al−Br)[b]	$\angle$(XAlY)[c]
AlF	1.671			
AlCl		2.135		
AlBr			2.318	
AlF^+	1.619			
$AlCl^+$		2.019		
$AlBr^+$			2.182	
AlF_2	1.659			149.32°
AlFCl	1.660	2.097		119.14°
AlFBr	1.663		2.270	118.73°
$AlCl_2$		2.096		118.82°
AlClBr		2.096	2.270	119.00°
$AlBr_2$			2.271	119.17°
AlF_2^+	1.606			$D_{\infty h}$
$AlFCl^+$	1.609	1.991		$C_{\infty v}$
$AlFBr^+$	1.612		2.144	$C_{\infty v}$
$AlCl_2^+$		1.997		$D_{\infty h}$
$AlClBr^+$		1.999	2.153	$C_{\infty v}$
$AlBr_2^+$			2.156	$D_{\infty h}$
AlF_3	1.645			D_{3h}
AlF_2Cl	1.646	2.062		$\angle(\mathrm{FAlCl}) = 120.66^\circ$
AlF_2Br	1.649		2.227	$\angle(\mathrm{FAlBr}) = 120.61^\circ$
$AlFCl_2$	1.649	2.066		$\angle(\mathrm{FAlCl}) = 119.45^\circ$
AlFClBr	1.651	2.066	2.231	$\angle(\mathrm{FAlBr}) = 119.26^\circ$ $\angle(\mathrm{ClAlBr}) = 121.34^\circ$
$AlFBr_2$	1.652		2.232	$\angle(\mathrm{FAlBr}) = 119.11^\circ$
$AlCl_3$		2.069		D_{3h}
$AlCl_2Br$		2.071	2.235	$\angle(\mathrm{ClAlBr}) = 120.20^\circ$
$AlClBr_2$		2.071	2.237	$\angle(\mathrm{ClAlBr}) = 119.84^\circ$
$AlBr_3$			2.238	D_{3h}
$AlF_2(\cdots F)^+$	1.611 × 2 (2.018)			$\angle(\mathrm{FAlF'}) = 100.13^\circ$ [d]
$AlF(\cdots F_2)^+$	1.606 (1.724 × 2)			$\angle(\mathrm{FAlF'}) = 145.31^\circ$ [d]
AlF_2Cl^+	1.618	2.296		$\angle(\mathrm{FAlCl}) = 105.83^\circ$
AlF_2Br^+	1.622		2.454	$\angle(\mathrm{FAlBr}) = 106.79^\circ$
$AlFCl_2^+$	1.621	2.009 (2.312)		$\angle(\mathrm{FAlCl}) = 148.37^\circ$ [d] $\angle(\mathrm{FAlCl'}) = 102.83^\circ$ [d]
$AlFBr(\cdots Cl)^+$	1.625	2.298	2.171	$\angle(\mathrm{FAlBr}) = 149.47^\circ$ $\angle(\mathrm{ClAlBr}) = 104.66^\circ$
$AlFCl(\cdots Br)^+$	1.626	2.012	2.474	$\angle(\mathrm{FAlCl}) = 145.96^\circ$ $\angle(\mathrm{ClAlBr}) = 110.77^\circ$
$AlFBr_2^+$	1.627		2.171 (2.472)	$\angle(\mathrm{FAlBr}) = 146.60^\circ$ [d] $\angle(\mathrm{BrAlBr'}) = 109.47^\circ$ [d]
$AlCl_3^+$		2.017 × 2 (2.320)		$\angle(\mathrm{ClAlCl'}) = 106.07^\circ$ [d]
$AlCl_2Br^+$		2.021	2.486	$\angle(\mathrm{ClAlBr}) = 107.30^\circ$
$AlClBr_2^+$		2.022	2.183 (2.479)	$\angle(\mathrm{ClAlBr}) = 146.19^\circ$ [d] $\angle(\mathrm{ClAlBr'}) = 104.67^\circ$ [d]
$AlBr_3^+$			2.217 (2.306 × 2)[e]	$\angle(\mathrm{BrAlBr'}) = 118.54^\circ$ [d]

[a] For bromine, the basis set employed[9] is the 641(d) basis of Binning and Curtiss.[12] [b] Internuclear separation, in angstroms. [c] Bond angle, in degrees. [d] The symbolism X′ is used to denote the halogen atom associated with the long Al−X bond. [e] B3-LYP/6-31G* geometry. See text for discussion.

of the discrepancy is not understood. Polychlorinated compounds are found to be significantly better treated by G2 theory when spin−orbit corrections are included.[9] Nevertheless, the original formulation of G2 theory,[4] including calibration of the empirical higher level correction, HLC, does not include spin−orbit corrections, and in the case of polyfluorinated compounds, the agreement with experiment is marginally poorer when atomic spin−orbit corrections are included.[9] Consequently, we have not included any consideration of spin−orbit effects for first- and second-row atoms in the ab initio values tabulated in this study.[10] In view of the findings of previous studies on the reliability of G2,[6,8,9] in particular concerning polyhalogenated species,[9] we ascribe a greater than typical uncertainty of ±20 kJ mol^{-1} to the G2 $\Delta H^\circ_{f,0}$ values determined in the present study. This may, indeed, be overcautious: note that the agreement which we find here, between G2 and experiment, is within ±13 kJ mol^{-1} for all eight species (AlF, AlCl, AlF^+, AlF_3, AlF_2Cl, $AlFCl_2$, $AlCl_3$, and $AlBr_3$) for which experimental values are themselves known to ±10 kJ mol^{-1} or better.

All calculations reported herein were performed using the GAUSSIAN94 suite of programs.[11]

Results and Discussion

Optimized geometries, obtained at the MP2(full)/6-31G* level of theory, are detailed in Table 1. G2 total energies and enthalpies of formation are presented in Table 2. Bond dissociation enthalpies and ionization energies are shown in Tables 3 and 4. We shall discuss below the various trends evident in the calculated values.

AlX. The present G2 results are in very good agreement with the literature values for the enthalpies of formation of AlF, AlCl, and AlBr. It is interesting to note that the calculated G2 $\Delta H^\circ_{f,0}$ values fall, in all three cases, close to the lower bounds of the literature values, although it is not possible to say whether this is a genuinely systematic effect or merely coincidence.

AlX^+. Calculated enthalpies of formation for the monohalide cations agree comfortably with the (rather uncertain) values listed in the 1985 JANAF tabulation.[3] There is also excellent agreement with the subsequent listing of $\Delta H^\circ_{f,0}(AlF^+) = 673.9$ kJ mol^{-1} in the NBS handbook of ion/neutral thermochemistry:[14] the latter value, derived from a determination of IE(AlF) = 9.73 ± 0.01 eV,[13] is almost identical to our G2 result.

TABLE 2: Total Energies and Enthalpies of Formation for Aluminum/Halide Species, at the G2 Level of Theory

species	ZPE,[a] mhartree	E_0,[b] hartree	$\Delta H°_{f,0}$,[c] kJ mol^{-1}	$\Delta H°_{f,0}$(lit),[d] kJ mol^{-1}
AlF		−341.821 27[e]	−271.5	−265.624 ± 3.35
AlCl		−701.800 18[e]	−58.7	−51.66 ± 6.3
AlBr	0.77	−2814.632 65	11.0	23.13 ± 12.55
AlF^+	2.05	−341.462 18	671.3	686.0 ± 24; 673.9 ± 4[f]
$AlCl^+$	1.28	701.457 93	839.9	855.7 ± 40
$AlBr^+$	1.00	−2814.296 73	893.0	[920.4][g]
AlF_2	4.22	−441.618 73	−626.4	−693 ± 40; [−749][g,h]
AlFCl	3.35	−801.601 72	−424.4	[−488.1 ± 63]
AlFBr	3.07	−2914.434 85	−356.3	
$AlCl_2$	2.50	−1161.585 24	−223.8	−279.4 ± 20
AlClBr	2.22	−3274.418 48	−156.0	
$AlBr_2$	1.93	−5387.251 80	−88.5	
AlF_2^+	4.97	−441.300 86	208.1	87 ± 63; [33][g]
$AlFCl^+$	4.05	−801.301 88	362.8	271 ± 126
$AlFBr^+$	3.74	−2914.140 66	416.1	
$AlCl_2^+$	3.16	−1161.300 54	523.7	475 ± 75
$AlClBr^+$	2.94	−3274.138 13	580.1	
$AlBr_2^+$	2.45	−5386.975 46	637.2	
AlF_3	7.47	−541.499 45[i]	−1200.0	−1205.60 ± 2.5
AlF_2Cl	6.47	−901.482 69	−998.7	−995.98 ± 6.3
AlF_2Br	6.11	−3014.314 46	−927.0	
$AlFCl_2$	5.47	−1261.465 70	−796.7	−788.4 ± 6
AlFClBr	5.12	−3374.297 51	−725.1	
$AlFBr_2$	4.77	−5487.129 44	−653.8	
$AlCl_3$	4.50	−1621.448 74[i]	−594.8	−582.85 ± 2.9
$AlCl_2Br$	4.14	−3734.280 75	−525.5	
$AlClBr_2$	3.78	−5847.111 48	−447.8	
$AlBr_3$	3.41	−7959.944 90	−382.3	−387.16 ± 1.7
$AlF_2(\cdots F)^+$	6.06[j]	−540.960 27[k]	215.6	[≤285][g]
$AlF(\cdots F_2)^+$	8.58	−540.959 43	217.8	[≤285][g]
AlF_2Cl^+	5.90	−901.031 29	186.5	
AlF_2Br^+	5.72	−3013.892 44	181.1	
$AlFCl_2^+$	4.94	−1261.024 17	362.6	
$AlFBr(\cdots Cl)^+$	4.53	−3373.861 89	418.6	
$AlFCl(\cdots Br)^+$	4.76	−3373.884 03	360.5	
$AlFBr_2^+$	4.37	−5486.719 89	421.5	
$AlCl_3^+$	3.95	−1621.016 32	540.6	[576][g]
$AlCl_2Br^+$	3.81	−3733.874 93	541.7	
$AlClBr_2^+$	3.42	−5846.711 36	601.0	
$AlBr_3^+$ [l]				[616][g]

[a] Zero-point energy (1 mhartree = 2.6255 kJ mol^{-1}) obtained as the corrected value from the HF/6-31G* geometry unless otherwise indicated. [b] Total energy including ZPE. [c] Enthalpy of formation at 0 K, with an ascribed uncertainty of ±20 kJ mol^{-1} (see text). [d] Experimental (0 K) enthalpy of formation where available, taken from the JANAF compendium[3] unless otherwise noted. [e] G2 result previously reported in ref 4. [f] Reference 13. [g] Reference 14. [h] Reference 15. [i] G2 result previously reported in ref 9. [j] Zero-point energy obtained at the MP2(full)/6-31G* level and scaled by a factor of 0.9427.[16] [k] G2(ZPE = MP2) value.[17] [l] See text for discussion.

The accord between G2 and experimental values for $\Delta H°_{f,0}(AlF^+)$ is especially gratifying since this is the *only* open-shell or cationic aluminum halide whose thermochemistry is experimentally well-established: we can, therefore, claim a modicum of confidence in the reliability of our calculations on the many other odd-electron or ionized halides included in the present study.

AlXY. The JANAF thermochemical tables list three such species, two of which (AlF_2 and AlFCl) are associated with very large uncertainties (of ±40 and ±63 kJ mol^{-1}, respectively).[3] Our G2 results disagree with the JANAF values for AlF_2 and $AlCl_2$, and the G2 and literature values for AlFCl agree only barely within the combined uncertainties.

There are several grounds for disputing the reliability of the JANAF values, even within the large uncertainties quoted. In all three instances, the JANAF $\Delta H°_{f,0}$ values adopted are chosen assuming that the average bond energies in the dihalides are equal to the average bond energies found for the analogous, well-characterized trihalides (with AlFCl compared to the median of the values for AlF_3 and $AlCl_3$). This disregards the observation that the JANAF-recommended bond energies for AlF, AlCl, and AlBr are all 60−80 kJ mol^{-1} higher than the average bond energies in AlF_3, $AlCl_3$, and $AlBr_3$: if the monohalide and trihalide bond energies differ by so much, why should the dihalide bond energies agree with either AlX or AlX_3? Indeed, it is intuitively reasonable to expect $D°_0(X_2Al{-}X)$ to exceed the average bond energy in AlX_3, since cleavage of the first bond in AlX_3 will produce a radical pair (which can also be seen as a factor in the high values for $D°_0(Al{-}X)$ for the monohalides): by this argument, the average bond energy in AlX_2 should be significantly lower than the average bond energy in AlX_3, which is indeed reflected in our G2 results. Woolf has noted[15] that such a reduction in bond energy, for odd-electron fluorides compared to even-electron fluorides, is evident in the fluorides of other group III and IVA elements for which sufficient data exist (namely B, C, Si, Ge, Sn, and Pb) and that the absence of this trend in the data for aluminum may be an artifact of the large uncertainty in $\Delta H°_f(AlF_2)$.[15]

The JANAF tables cite several experimental studies as support for their recommended values for the dihalides. Only for $AlCl_2$ do the various experimental results[18−22] cluster around a common value (which makes the discrepancy between G2 and JANAF for $AlCl_2$ rather more difficult to account for). For AlF_2, the range of literature $\Delta H°_{f,298}$ values encompasses −787 to −633 kJ mol^{-1};[21−23] perhaps significantly, the value of

TABLE 3: Bond Dissociation Enthalpies and Ionization Energies of Neutral Aluminum/Halide Species, at the G2 Level of Theory

species	$D°_0$ (Al−F)[a]	$D°_0$ (Al−Cl)[a]	$D°_0$ (Al−Br)[a]	IE[b]	IE(lit)[c]
AlF	676.0			9.771	9.73 ± 0.01[d]
AlCl		505.6		9.313	9.4
AlBr			434.0	9.141	[9.3]
AlF_2	432.3			8.650	[8.1± 0.9]
AlFCl	443.0	272.6		8.159	[7.9 ± 1.0]
AlFBr	444.7		202.7	8.005	
$AlCl_2$		284.7		7.747	[7.8 ± 0.9]
AlClBr		286.7	215.1	7.629	
$AlBr_2$			217.4	7.920	
AlF_3	650.9			14.672	≤15.45[e]
AlF_2Cl	651.5	491.8		12.283	
AlF_2Br	647.9		418.4	11.484	
$AlFCl_2$	650.2	491.9		12.015	
AlFClBr	646.4	488.4	418.6	11.251	
$AlFBr_2$	642.8		415.4	11.144	
$AlCl_3$		490.6		11.767	[12.01][e]
$AlCl_2Br$		487.4	417.8	11.043	
$AlClBr_2$		480.6	411.3	10.888	
$AlBr_3$			411.5		[10.4][e]

[a] Bond dissociation energy (0 K), in kJ mol^{-1}, obtained from the G2 total energies reported herein. [b] Calculated ionization energy, in eV. [c] Literature value of the ionization energy, from ref 4 unless otherwise indicated. [d] Reference 13. [e] Reference 14.

TABLE 4: Bond Dissociation Enthalpies of Aluminum/Halide Cations, at the G2 Level of Theory

species	$D°_0$ (Al−F)[a]	$D°_0$ (Al−Cl)[a]	$D°_0$ (Al−Br)[a]
AlF^+	305.4		
$AlCl^+$		179.2	
$AlBr^+$			124.3
AlF_2^+	540.5		
$AlFCl^+$	554.3	428.1	
$AlFBr^+$	554.3		373.1
$AlCl_2^+$		435.8	
$AlClBr^+$		432.6	377.7
$AlBr_2^+$			373.8
AlF_3^+	69.8		
AlF_2Cl^+	253.6	141.2	
AlF_2Br^+	312.3		145.0
$AlFCl_2^+$	238.4	119.9	
$AlFClBr^+$	296.2	175.2	120.2
$AlFBr_2^+$	293.0		112.6
$AlCl_3^+$		102.8	
$AlCl_2Br^+$		158.0	99.8
$AlClBr_2^+$		155.6	96.8
$AlBr_3^+$			20.1[b]

[a] Bond dissociation energy (0 K), in kJ mol^{-1}, obtained from the G2 total energies reported herein. [b] Value obtained using $E_e(AlBr_3^+)$ (B3-LYP/6-31G*-optimized geometry) and $E_e(AlBr_2^+)$.

$\Delta H°_{f,298} < -633$ kJ mol^{-1}, which agrees within the stated uncertainty with our G2 value of $\Delta H°_{f,0} = -626.4$ kJ mol^{-1}, is derived from a study[23] of the equibrium

$$AlF_{(g)} + AlF_{3(g)} \leftrightarrow 2AlF_{2(g)} \qquad (1)$$

whereas the other experimental determinations,[21,22] which show marked disgreement with each other *and* with the JANAF-recommended value as well as with the G2 value, are obtained from the equilibrium

$$2AlF_{(g)} \leftrightarrow Al_{(g)} + AlF_{2(g)} \qquad (2)$$

In all instances (and true, also, for the measurements on $AlCl_2$), the 0 K and room-temperature thermochemical parameters are extrapolated from the results of reaction studies at temperatures always exceeding 1100 K. In fact, the JANAF value[3] for $\Delta H°_{f,298}(AlF_2)$ does not agree with any of the previous experimental determinations[21−23] but is supported solely by the average bond-strength arguments described above; the same holds true for AlFCl, for which the sole experimental determination[21] (again, the result of a high-temperature equilibrium study) is $\Delta H°_{f,298} = -597$ kJ mol^{-1}. The JANAF tabulation[3] notes that all of the experimental results of Farber and co-workers,[18,20−22] applicable to AlF_2, AlFCl, and $AlCl_2$, may be associated with a negative bias in the derived $\Delta H°_{f,298}$ values due to uncertainties in the ionization energy used in these experiments. This is in accord with our observations that the G2 enthalpies are uniformly much higher than the values of Farber et al.,[18,20−22] although we would argue that the JANAF recommendations[3] for the enthalpies of these compounds are also significantly too low.

A possible criticism of the G2 results is that the aluminum dihalides are radicals and G2 is often found to perform rather poorly for odd-electron species: however, it has also been noted that agreement between G2 and well-characterized experimental values is generally good provided that the radicals being studied have little spin contamination.[24] In the present study, expectation values, $\langle S^2\rangle$, found for the dihalides were all very close to the value of 0.75 expected for "pure" doublet states, indicating that spin contamination is not a significant problem for these species. We infer from this that the G2 results for all of the dihalides, including those for which no experimental determinations have been performed, should be inherently reliable. We conclude by strongly recommending that the thermochemistry of the aluminum dihalides be subjected to further experimental study in order to resolve the dispute between literature and G2 results for these species.

$AlXY^+$. As noted in the Introduction, the JANAF enthalpies of formation for AlF_2^+, $AlFCl^+$, and $AlCl_2^+$ are all associated with very large uncertainties.[3] Perhaps not surprisingly, agreement between G2 and literature values is rather poor: the G2 results for $AlFCl^+$ and $AlCl_2^+$ lie far from the baselines of the recommended JANAF values, although agreeing within the combined uncertainties, while G2 and JANAF disagree strongly on $\Delta H°_{f,0}(AlF_2^+)$.

The experimental values of $\Delta H°_{f,0}(AlF_2^+)$ and $\Delta H°_{f,0}(AlCl_2^+)$ are derived from a study of the electron-impact dissociative ionization process

$$AlX_{3(g)} + e \leftrightarrow AlX_2{}^+{}_{(g)} + X_{(g)} + 2e \qquad (3)$$

In the JANAF tabulations, the experimental electron-impact appearance potentials, $AP(AlX_2^+/AlX_3)$, are held to contain a contribution from excess energy, by analogy with the appearance potentials $AP(BF_2^+/BF_3)$ and $AP(BCl_2^+/BCl_3)$ for which photoionization thresholds are found to lie between 0.4 and 0.9 eV below the corresponding electron-impact thresholds. The values that JANAF recommends for AlF_2^+ and $AlCl_2^+$ are based on estimated excess energies, in the appearance potentials for dissociative electron impact, of 1.0 ± 0.5 and 1.2 ± 0.6 eV, respectively. It should be stressed, first, that there is no direct evidence for excess energy in the electron-impact values of $AP(AlX_2^+/AlX_3)$ and, second, that the JANAF tabulation assumes, without apparent justification, that the excess energy for electron-impact dissociative ionization of AlF_3 and $AlCl_3$ is greater than that observed for the analogous boron trihalides. If the appearance potentials are used to determine $\Delta H°_{f,0}(AlXY^+)$ without correction for "excess energy", significantly better agreement is obtained for AlF_2^+ and $AlFCl^+$ (which in

JANAF is estimated, in the same manner as used for AlFCl$^•$, from the Al−F and Al−Cl bond energies in the homogeneous dihalide cations) but not for $AlCl_2^+$.

The near-perfect agreement seen in Table 3, between G2 and literature[3] values for IE($AlCl_2$), is merely fortuitous, since the JANAF enthalpies of formation for both $AlCl_2$ and $AlCl_2^+$ are substantially different from the G2 values; furthermore, the quantity IE($AlCl_2$) has never been measured directly, and we would argue that its derivation in the JANAF tables[3] involves a number of questionable or incorrect assumptions.

None of the bromine-containing dihalide cations appears to have been the subject of previous study: thus, calculated enthalpies of formation for $AlXBr^+$ (X = F, Cl, Br) cannot be adequately assessed. Nevertheless, we see no reason at present to question the reliability of these G2 values.

AlXYZ. Accurate experimental thermochemical values (i.e., uncertainties of ±3 kJ mol^{-1} or less) are available for the homogeneous trihalides AlF_3, $AlCl_3$, and $AlBr_3$, with slightly less precise values available for the mixed halides AlF_2Cl and $AlFCl_2$.[3] For all five species, G2 and literature values are in good agreement. We are confident, therefore, that the G2 enthalpies of formation for five other mixed halides (which have not yet been the subject of experimental study) are of similarly high quality.

AlXYZ$^+$. In the JANAF and NBS themochemical tabulations, estimated enthalpies of formation are available only for the homogeneous trihalide cations AlF_3^+, $AlCl_3^+$, and $AlBr_3^+$. Our G2 enthalpies for AlF_3^+ and $AlCl_3^+$ are lower than the literature values, in accordance with the expectation that the experimental values represent "vertical" ionization processes rather than "adiabatic" production of the ion in its preferred equilibrium geometry. Large "kinetic shifts" of this type are known also for several polyhalogenated cations such as CF_3^+ and SF_5^+.[25−27] As a test of the existence of large differences between vertical and adiabatic appearance potentials, we have also obtained G2 E_e values (lacking ZPE) for AlX_3^+ (X = F, Cl, Br) constrained at the respective neutral AlX_3-optimized geometries, as follows: $E_e(AlF_3^+) = -540.936\,62$ hartrees; $E_e(AlCl_3^+) = -1621.014\,53$ hartrees; and $E_e(AlBr_3^+) = -7959.519\,77$ hartrees, yielding vertical ionization energies of 15.519, 11.938, and 11.661 eV, respectively. These calculated vertical ionization energies are close to the experimental ionization energies for AlF_3 and $AlCl_3$; the calculated vertical IE of $AlBr_3$ is much higher than the experimental IE($AlBr_3$) $\sim$ 10.4 eV.[14] We shall comment on $AlBr_3^+$ in further detail below. The difference in vertical and adiabatic ionization energies for AlF_3^+ and $AlCl_3^+$ corresponds to kinetic shifts of ∼0.8 and ∼0.2 eV, respectively, for these ions. These are well within the range of kinetic shifts which have been observed for perfluorinated and perchlorinated cations.[14]

A fundamental difference between the $AlXYZ^+$ structures and all others incorporated in the present survey is that the $AlXYZ^+$ species generally possess one "long" and two "short" aluminum−halide bonds (apparent exceptions are $AlBr_3^+$ and one isomer of AlF_3^+). This observation, as well as Mulliken atom charges, indicates that the ion structures are best represented as $XYAl^+\cdots Z$, with the Al−Z bond typically ∼0.2 Å longer than expected. The identity of the "leaving group" Z in mixed halide cations is most often Br, although a relatively high-energy minimum is also found for the species $FBrAl^+\cdots Cl$, and Cl is invariably preferred as the leaving group in those cations containing only Cl and F.

Our calculations have located two structures, $AlF_2(\cdots F)^+$ and $AlF(\cdots F_2)^+$, as local minima upon the AlF_3^+ potential energy surface at the MP2(full)/6-31G* level of theory. The difference in energy between these two isomers is exceptionally small (∼2 kJ mol^{-1}) according to G2 theory: we find the structure $AlF2(\cdots F)^+$ to be the global minimum, in keeping with the structures obtained for other $AlXYZ^+$ species, but this ordering of isomers could feasibly be reversed at higher levels of theory. The $AlF(\cdots F_2)^+$ structure is notable for a F−F interatomic separation which, at 1.962 Å, is unexpectedly short—for comparison, the F−F distance in AlF_3 is 2.849 Å according to our MP2(full)/6-31G* calculations, while the bond lengths in F_2 and F_2^- are 1.421 and 1.891 Å, respectively, at this level of theory. The similarity with the F_2^- bond length and the examination of the Mulliken atomic charges in $AlF(\cdots F_2)^+$ suggest that the $AlF(\cdots F_2)^+$ structure is reasonably well represented as an electrostatic complex of Al^{3+}, F^-, and F_2^-.

Our results for $AlBr_3^+$ also require comment. Attempts to obtain an optimized geometry at the HF/6-31G* and MP2(full)/6-31G* levels were unsuccessful, with all initial guesses leading to dissociated $AlBr_2^+$ and Br. A structure for $AlBr_3^+$ was located upon the B3-LYP/6-31G* potential energy surface, but this structure (featuring one short and two long Al−Br bonds) was found to correspond to a transition state at the HF/6-31G* level of theory. G2 calculations yield a total E_e (excluding ZPE) of $-7959.521\,92$ hartrees for the B3-LYP-optimized structure, only 2.15 mhartrees (5.7 kJ mol^{-1}) below the corresponding E_e value for the vertically ionized $AlBr_3$ structure. We have also performed G2 calculations on an "estimated" structure for $AlBr_3^+$, having the geometric parameters $r(Al-Br) = 2.171$ Å, $r(Al-Br') = 2.479$ Å, and $\angle(BrAlBr') = 106.9°$: these parameters represent the values expected by comparison with other ions of the formulas $AlXYBr^+$ and $AlXBr_2^+$. This estimated geometry (which at the MP2(full)/6-31G* level led to Al−Br dissociation, as with the other initial guesses) yielded an E_e value of $-7959.513\,75$ hartrees; i.e., this geometry is higher in energy (by 6.02 and 8.17 mhartrees, respectively) than both the vertically ionized $AlBr_3$ structure and the B3-LYP-optimized geometry. We conclude, in light of the difficulties encountered in obtaining optimized geometries and in view of the significant discrepancy between calculated and experimental thermochemical values, that $AlBr_3^+$ is not well treated by G2 theory. It would appear that the ionization energy of $AlBr_3$ requires further experimental and theoretical investigation in order to properly resolve this matter.

General Trends in Bond Energies and Ionization Energies. The most strikingly apparent trend evident from a perusal of Tables 3 and 4 is that, for any homologous series of aluminum halides, the bond dissociation enthalpies obey the relation $D°_0(Al-F) > D°_0(Al-Cl) > D°_0(Al-Br)$. This is clearly consistent with a stronger electrostatic interaction between Al^{n+} and the smaller fluoride anion in these largely ionic compounds.

Closer examination of Table 3 suggests that the empirical relation $D°_0(Al-F) - 160$ kJ mol^{-1} $\sim D°_0(Al-Cl) \sim D°_0(Al-Br) + 70$ kJ mol^{-1}, for any homologous series of neutral aluminum halides X_iY_jAlF, X_iY_jAlCl, and X_iY_jAlBr (X, Y = F, Cl, Br; $i, j = 0, 1$), may be surprisingly useful as a predictor of aluminum/halogen atom bond strengths in unknown aluminum halides. A similar empirical rule, yielding $D°_0(Al-F) - 120$ kJ mol^{-1} $\sim D°_0(Al-Cl) \sim D°_0(Al-Br) + 55$ kJ mol^{-1}, can be obtained for aluminum halide cations from the data shown in Table 4, except that the bond strength of AlF_3^+ is found to be unexpectedly low. The low value of $D°_0(F_2Al^+-F)$ may be connected with the high electronegativity of the fluorine atom: if we consider the $FAlF^+$ cation as a purely electrostatic complex $[F^-\cdots Al^{3+}\cdots F^-]$,[28] we can interpret the low AlF_3^+ bond strength (and long $F_2Al^+\cdots F$ bond) as a consequence of the weak affinity of Al^{3+}, in AlF_2^+, for yet another electron-withdrawing fluorine atom. It should be noted that the phenomenon of exceptionally low $D°_0(F_nM^+-F)$ values is also apparent for other highly fluorinated cations such as CF_4^+ and SF_6^+.[29,30]

Another trend apparent in the G2 results is that, for radicals or cations, the aluminum/halogen atom bond strength is somewhat sensitive to the identity of the other atoms present: this is not the case for the closed-shell, neutral trihalides. For example, among the dihalide radicals AlXY, the Al−F, Al−Cl, and Al−Br bonds are all ~12 kJ mol^{-1} weaker when the other halogen atom present is F than when this atom is Cl or Br. The effect is similar, but more erratic, for the dihalide cations $AlXY^+$, while for the trihalide cations $AlXYZ^+$ the presence of fluorine atoms strengthens the other bonds present (except, as noted above, for $D°_0(F_2Al^+-F)$ in AlF_3^+).

It is of some concern that the G2 value for $AlBr_3^+$ appears inherently unreliable, as detailed above: this is one of only three aluminum trihalide cations to have been studied experimentally, so the calculated thermochemical values for other $AlXYZ^+$ species are also somewhat questionable by implication. We do not believe, however, that the calculated values for the other trihalide cations are problematic: $AlBr_3^+$ is notable for difficulties encountered in attempted optimization, while the other $AlXYZ^+$ species possess well-defined optimized geometries. Furthermore, a trend (consistent if $AlBr_3^+$ is excluded) is apparent for the calculated ionization energies of AlXYZ: progressive substitution of F by Cl, or of Cl by Br, leads to a steady and apparently systematic reduction in IE(AlXYZ). A similar trend is seen in the experimental ionization energies of the perhalomethanes $CF_iCl_jBr_k$ $(i + j + k = 4)$.[14] In the present study, it is notable that the calculated ionization energies for $AlCl_2Br$ (11.043 eV) and $AlClBr_2$ (10.888 eV) are not greatly above the literature value of IE($AlBr_3$) ~ 10.4 eV so that the observed trend in calculated ionization energies appears to be consistent with the literature value for IE($AlBr_3$) even if the G2 value for this particular parameter is questionable. We conclude that the G2 values for the other aluminum trihalide cations are probably reliable: the paucity of experimental data on this class of cations precludes a more definite assessment.

Conclusions

Only eight aluminum halides have $\Delta H°_{f,0}$ values that are currently known to an accuracy of ±10 kJ mol^{-1} or better. Our calculated G2 enthalpies of formation are in good agreement with all eight members of this “test set”. In contrast, G2 produces $\Delta H°_{f,0}$ values that are in strong disagreement with the JANAF-recommended values for AlF_2, $AlCl_2$, and AlF_2^+; the G2 and JANAF values for AlFCl, $AlFCl^+$, and $AlCl_2^+$ are also notably disparate but encompassed by very large experimental uncertainties. Based on G2’s good performance for the aluminum halide test set, we urge an experimental reevaluation of the thermochemistry of neutral and cationic aluminum dihalides.

Large differences are also noted between the calculated and literature values of $\Delta H°_{f,0}(AlF_3^+)$ and $\Delta H°_{f,0}(AlBr_3^+)$. In the case of AlF_3^+, the discrepancy is attributable to a sizable kinetic shift between vertical and adiabatic ionization energies of AlF_3 (a smaller kinetic shift is found also for $AlCl_3^+$, for which the difference between calculated and literature values is significantly smaller). The theoretical treatment of $AlBr_3^+$ appears to be unsatisfactory: the calculated vertical ionization energy of $AlBr_3$ is 1.26 eV higher than the literature value, and all efforts to obtain an optimized geometry (similar to that found for the other trihalide cations) were unsuccessful.

A majority of the species included in the present study have not previously been investigated: the G2 results for such species cannot therefore be properly assessed at present. We would anticipate, however, that our present results for these species are inherently reliable, at least to within the (conservatively large) stated uncertainty of ±20 kJ mol^{-1}.

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References and Notes

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