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BAC-G2 Predictions of Thermochemistry for Gas-Phase Aluminum Compounds

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A self-consistent set of thermochemical data for 55 molecules in the Al−H−C−O−F−Cl system are obtained from ab initio quantum-chemistry calculations using the BAC-G2 method. Calculations were performed for both stable and radical species. Good agreement is found between the calculations and experimental heats of formation in most cases where data are available for comparison. Electronic energies, molecular geometries, moments of inertia, and vibrational frequencies are provided in the Supporting Information, as are polynomial fits of the thermodynamic data (heat of formation, entropy, and heat capacity) over the 300−4000 K temperature range.

I. Introduction

Chemical vapor deposition (CVD) of aluminum and aluminum compounds is of interest for a variety of technologies. For example, formation of conduction lines in the fabrication of microelectronic devices is a well-established technology. CVD processes are also being developed to produce thermal barrier coatings, alumina-based ceramics, and hard coatings for abrasion and corrosion resistance. The formation of volatile aluminum compounds is also a key element in plasma etching processes. Accurate thermochemical data (2 kcal mol^{-1} or better) for gas-phase species, in the form of heats of formation, heat capacities, and entropies, are an essential element in the development of computational models used to simulate CVD processes. Unfortunately, such data are often not available, particularly when organic ligands are involved. Group III compounds (i.e., those containing B, Al, Ga, In, or Tl) are typical in this regard, in that reliable thermochemistry is generally available in standard compilations[1−4] for only the closed-shell halides.

Theoretical methods can be of great value in filling the many gaps that exist in thermochemical databases.[5] Among the many ab initio techniques that have been developed during the past 15 years is G2,[6,7] a composite method that combines a series of calculations with empirical corrections to simulate a higher level of theory. This method has been used successfully to predict heats of formation for compounds in the first and second rows; for a standard test set of 148 molecules, the average deviation from experiment is 1.58 kcal mol^{-1}, with a maximum deviation of 8.2 kcal mol^{-1}.[7] Accuracies at this level are necessary for such data to be useful for CVD model development. The accuracy of the G2 method for many classes of compounds relevant to CVD has not been established, however. For example, we are unaware of any application of G2 to group III organometallic compounds, whose use as CVD precursors is common, because films can be deposited at lower temperatures than are typically required when halogenated precursors are used.

We recently developed a modification of the G2 method known as BAC-G2[8] (bond-additivity-corrected G2) that incorporates additional empirical corrections that further improve the accuracy of G2. While such improvements are in many cases unnecessary for small molecules, such as those included in the standard G2 test set,[7] they become increasingly important in larger molecules where the accumulation of errors can decrease the accuracy of thermodynamic predictions significantly. These corrections also yield more accurate heats of formation for an important class of CVD precursors, halide compounds, for which the G2 method performs poorly.[9,10] In this paper, we report BAC-G2 predictions of heats of formation and bond energies for compounds containing aluminum. The literature contains several reports of thermodynamic data for aluminum-containing species using theoretical methods, including a recent investigation using the G2 method by Swihart and Catoire.[11] Our investigation focuses on the thermochemistry of monomeric aluminum compounds containing bonds to H, CH_3, OH, F, and Cl and includes many species not treated in earlier work. In addition to reporting the heats of formation for 55 molecules, we discuss bond energies for many of the compounds examined and trends exhibited by the various homologous series within the set. This work expands and completes two preliminary investigations published earlier by us.[12,13]

II. Theoretical Methods

A. Overview of the BAC-G2 Method. The BAC-G2 method applies the BAC corrections to the standard G2 method,[6] using Gaussian-94.[14] The electronic-structure calculations to determine the geometry, vibrational frequencies, and electronic energies are the same as those in the G2 method. Specifically, the geometry and vibrational frequencies in the BAC-G2 method are obtained from a Hartree−Fock (HF) calculation (restricted

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Hartree–Fock, RHF, for closed shell molecules and unrestricted Hartree–Fock, UHF, for open shell molecules) using the 6-31G-(d) split-valence basis set with polarization functions on the heavy atoms. At this level of theory, vibrational frequencies are systematically too large compared to experimental values. We therefore scale the HF harmonic frequencies downward by 12%. The electronic energies at the QCI, MP4, and MP2 levels of theory, as well as the collective G1, G2MP2, and G2 electronic energies, are taken directly from the output of the G2 method. The basis sets are the same as those defined in the standard G2 method. The geometry used in the single-point calculations is obtained by reoptimizing the HF geometry at the MP2 level, again as defined in the G2 method.

The BAC corrections for the BAC-G2 method are those defined previously.[8] Briefly, three types of corrections (E_{BAC-}; units of energy) are used: atomic, molecular, and bondwise, indicated in eqs 1–4 below. The atomic correction depends on the atom type:

$$E_{BAC-atom} = \sum_k E_{BAC-atom}(A_k) \tag{1}$$

where the sum runs over all the atoms in the molecule. The value of $E_{BAC-atom}(A_k)$ depends on the atom type, and A_k is an adjustable parameter.

The molecular BAC correction arises from errors in the overall electronic structure of the molecule. The BAC correction for this term is given by

$$E_{BAC-molecule} = E_{BAC-elecpair} \tag{2}$$

where $E_{BAC-elecpair}$ depends on the difference between the spin of the molecule and the sum of the spins of the constituent atoms:

$$E_{BAC-elecpair} = K_{elecpair}\,(\text{spin}_{molecule} - \sum_{atom} \text{spin}_{atom}) \tag{3}$$

where $K_{elecpair}$ is an empirically adjusted parameter for a given BAC method and "spin" refers to the S quantum number.

The third type of BAC correction depends on the formation of chemical bonds. In this instance, we distinguish between bonds and pairwise interactions. A bond is taken to mean the formation of an electron pair between the atoms. This correction addresses systematic errors arising from electron-pairing not covered by eq 3. The correction for each bond A–B in the molecule having neighbors C and D (e.g., C–A–B–D) is given by

$$E_{BAC-bond}(AB) = A_{AB}e^{-\alpha R_{AB}} + \sum_C B_{CA} + \sum_D B_{DB} \tag{4}$$

where the first term is the correction for the bond alone, while the corrections for its nearest neighbors are treated as a sum of corrections for each neighbor of the form

$$B_{CA} = B_C + B_A \tag{5}$$

The B_A's are constants that depend only on the type of atom. The bond-distance dependence in eq 4 exists only in the first term for the bond itself. Furthermore, α no longer depends on the type of bond, as it did in the original BAC method.[15] Note that the bondwise corrections do not go to zero at infinity, due to the terms $\Sigma B_{CA} + \Sigma B_{DB}$ defined by eq 4.

The parameters for each of the corrections are given in Table 1; values of all parameters with the exception of those for aluminum (see below) were determined previously.[8] The atomic corrections (eq 1) are straightforward. For the bondwise corrections (eq 4), the α exponent is taken to be 3.0 Å^{-1}, while the preexponential coefficient A_{AB} is taken to be the geometric mean of the individual atom types, i.e.,

TABLE 1: BAC-G2 Parameters (Energies, kcal mol^{-1}) $K_{elec\ pair} = 0.860$ for all calculations.

atom	A_{atom}	B_{atom}	A_{ii}
H	0.485	−0.146	1.462
C	1.081	0.051	0.0
N	1.498	−0.010	2.281
O	−0.501	−0.010	114.3
F	−1.942	0.215	373.1
Al	−1.500	0.000	300.0
Cl	−0.776	0.087	1433.7

$$A_{AB} = -(A_{AA}A_{BB})^{1/2} \tag{6}$$

Equation 4 also includes contributions from the nearest-neighbor B_{ij} terms (defined by eq 5). The accuracy of the parameters comprising these terms (see Table 1) is difficult to assess because of their small size. This is due to the fact that to date we have only applied the BAC-G2 method to relatively small molecules (less than seven heavy, i.e., non-hydrogen, atoms), for which accurate experimental thermodynamic data exist. However, these terms become quite significant for larger molecules and for halides (see below). Unfortunately, given the limited accuracy of experimental data for larger non-hydrocarbon, unsaturated gas-phase species, it will remain difficult to establish the accuracy of the B_{atom} terms.

The corrected heat of formation at 0 K ($\Delta H_f{}^\circ{}_0$) can now be obtained from the calculated electronic energy. First, the electronic energy is added to the zero-point energy (which is automatically included in the G2(0K) output of the Gaussian-94 code). Next, the resulting energy is subtracted from the electronic energies of the atoms to give an electronic heat of atomization:

$$E_{atomization} = \sum_i^n E_i(\text{atoms}) - (E_{ab\ initio}(\text{molecule}) + E_{ZPE}) \tag{7}$$

Referencing this energy against the experimental $\Delta H_f{}^\circ{}_0$ at 0 K of the atoms (given in Table 3) in the gas phase yields the uncorrected $\Delta H_f{}^\circ{}_0$:

$$\Delta H_f{}^\circ{}_{0,uncorrected} = \sum_{atoms} \Delta H_f{}^\circ{}_{0,atoms} - E_{atomization} \tag{8}$$

Subtracting the BAC corrections from this energy finally yields $\boldsymbol{\Delta} H_f{}^o{}_0$ at 0 K:

$$\Delta H_f{}^o{}_{0,BAC} = \Delta H_f{}^o{}_{0,uncorrected} - E_{BAC-correction} \tag{9}$$

Heats of formation, entropies, and free energies at various temperatures are then obtained using equations derived from statistical mechanics (the same procedure as in the original BAC-MP4 method, which includes corrections for free rotors, such as CH_3 groups).[15] Thus, for finite temperatures, the raw G2 energies (without BAC corrections) obtained from the BAC-G2 method do not correspond to those from the output of a Gaussian G2 calculation, since hindered rotors are included in the BAC procedure.

Using an ad hoc expression similar to that formulated for the earlier BAC-MP4 method,[15,16] we obtain an estimate of the error (or confidence level) in the BAC-G2 method. In this case, we use the similarities between the G1 and G2-MP2 methods and the G2 method itself as an indication of the error:

$$\text{error}(\text{BAC}-\text{G2}) = \text{sqrt}\{(1.0\ \text{kcalmol}^{-1}) + (\Delta H_{\text{BAC}-\text{G2}} - \Delta H_{\text{BAC}-\text{G2MP2}})^2 + (\Delta H_{\text{BAC}-\text{G2}} - \Delta H_{\text{BAC}-\text{G1}})^2\} \quad (10)$$

B. Determination of BAC Parameters for Aluminum. The BAC parameters for aluminum were determined by optimizing the heats of formation predicted by BAC-G2 for a set of aluminum compounds whose heats of formation are considered well-known. The compounds used are the trivalent species AlH_3, AlF_3, and $AlCl_3$, the diatomics AlH, AlF, and AlCl, as well as the constituent atoms. The parameters in Table 1 represent a compromise that yields the best overall accuracy (predicted heats of formation within ±2 kcal mol^{-1} of accepted experimental values) for these species.

Note that, in contrast to the original BAC-MP4 method,[15,16] in which the heat of formation for isolated atoms was set to the experimental value, the atomic heats of formation obtained from the BAC-G2 method differ somewhat from the experimental values. For example, the BAC-G2 heat of formation for Al(g) is 80.144 kcal mol^{-1} at 298 K, while Gurvich et al. report 78.87 ± 0.71 kcal mol^{-1}.[2] This difference results from the fact that the objective of the BAC-G2 method is to obtain accurate heats of formation for molecular species, which are the data most often needed for practical problems. Thus, some of the systematic error in the G2 calculation is shifted into the predictions for the atoms in order to obtain better agreement with well-established molecular heats of formation.

III. Results

A. Heats of Formation and Bond Dissociation Energies. Results of applying the BAC-G2 method to species in the Al−H−C−O−F−Cl system are presented in Tables 2−6, which list the atomic (eq 1), molecular (eq 2), and bondwise (eq 4) corrections for all molecules examined (Table 2); heats of formation at 0 K ($\Delta H_f\,^o(0K)$) at various levels of theory, as well as the atomization energy at the BAC-G2 level (ΣD_0; Table 3); $\Delta H_f\,^o(298K)$ and references to values from experiments and theory in the literature (Table 4); thermodynamic parameters at various temperatures (Table 5); and selected bond dissociation energies at 298 K (Table 6). In the Supporting Information (Tables S7− S11), we also provide raw electronic energies at the G2 level, atomic coordinates, vibrational frequencies, moments of inertia, and polynomial fits of the thermodynamic data suitable for use with the CHEMKIN software.[17] As has been typical in previous publications involving the BAC-MP4 series,[15,16,18−25] we focus our discussion on the predicted thermochemical parameters, rather than on the ab initio calculations themselves.

Table 3 reveals the trend toward convergence in each molecule as the level of theory increases from BAC-QCI to BAC-G2. In most cases, the calculation appears to be converged at the BAC-G2MP2 level, there being little difference in the heats of formation predicted at the BAC-G2MP2 and BAC-G2 levels. Exceptions to this almost exclusively involve fluorinated compounds. For example, the heat of formation of AlF_3 at the BAC-G2 level is 8.5 kcal mol^{-1} lower than at the BAC-G2MP2 level. This behavior is reflected in the relatively large uncertainty in the predicted heats of formation of the fluorinated species (Table 4). Table 3 also indicates that differences between BAC-G2 predictions and G2 itself are, for the most part, small. The largest difference, 2.6 kcal mol^{-1}, is for $Al(CH_3)_3$, which might be expected since this is the largest molecule included in the study. As discussed above, it is in the prediction of thermochemistry for large polyatomics where the value of the BAC approach is expected to be most clear. Finally, Table 3 includes the BAC-G2 atomization energies (ΣD_0; calculated from the BAC-G2 molecular heats of formation and the experimental[1] atomic heats of formation at 0 K) for comparison with the results of other computational studies in which the heat of formation was not calculated.

Trends in heats of formation (298 K) as a function of the number of ligands of a specific type are shown in Figures 1−4. There are several noteworthy observations. The most general one is that, in all cases, replacement of one ligand with another within a homologous series (i.e., AlX_nY_{3-n}, $n = 0-3$) results in a linear change in the heat of formation. Deviations from perfect linearity (based on a least-squares fit) are less than 1 kcal mol^{-1} in most cases. The series closest to perfect linearity is $AlH_n(CH_3)_{3-n}$ (maximum deviation < 0.1 kcal mol^{-1}), while those displaying the largest deviations are $AlCl_n(CH_3)_{3-n}$ and AlH_nF_{3-n} (maximum deviation ∼ 2 kcal mol^{-1}). This confirms the essentially local nature of the bonding within these compounds; i.e., the interaction between aluminum and a given atom or group is largely unaffected by its neighbors, while confirming that interactions between chlorine and methyl groups may occur, as was observed previously in silicon compounds.[19] It is unclear whether the higher deviation seen for the fluorine substitution of hydrogen is due to nonlocalized bonding or poor performance of the G2 method. Notably, however, the $Al(OH)_nF_{3-n}$ and $AlCl_nF_{3-n}$ series both have low maximum deviations (<0.5 kcal mol^{-1}), suggesting that the nonlinearity is due to a bonding interaction in the aluminum fluorohydrides and not to the G2 method itself. We have found few exceptions to linearity in our previous examinations of group III and group IV chemistry; examples include the $SiH_{4-n}(OH)_n$[20] and $SiCl_{4-n}(CH_3)_{4-n}$[19] homologous series.

The remaining conclusions we draw from Figures 1−4 concern the relative molecular stability induced by the various ligands. First, as can be seen in Figure 1, replacing H with any of the other four ligands (CH_3, OH, F, or Cl) results in increased molecular stability, since the heat of formation always decreases as the number of non-hydrogen ligands increases. The slopes of the four lines in Figure 1 are −106.2 kcal mol^{-1} for substitution by F, −88.3 kcal mol^{-1} for substitution by OH, −57.5 kcal mol^{-1} for substitution by Cl, and −14.6 kcal mol^{-1} for substitution by CH_3. In contrast, substitution of OH by anything except F results in molecular destabilization, since the heats of formation increase with increasing numbers of non-OH ligands (Figure 2). Replacing OH with F decreases ΔH_f° by 17.8 kcal mol^{-1}. Trends produced by replacing CH_3 (Figure 3) and Cl (Figure 4) fall between these extremes. For example, replacing Cl by either OH or F results in stabilization, by 30.8 and 48.5 kcal mol^{-1}, respectively. Thus, as one might expect, the overall trend in molecular stability is F > OH > Cl > CH_3 > H.

Bond dissociation energies (BDE), which can be calculated from the molecular and atomic heats of formation given in Table 4, generally reflect the trends in heats of formation discussed above. The calculations predict increasing Al−ligand bond strengths in the order H ∼ CH_3 < Cl < OH < F. For trivalent species, the Al−H and Al−CH_3 bond energies are comparable, falling in the range of 83−88 kcal mol^{-1}. Bonds to Cl are considerably stronger, with values of 118−125 kcal mol^{-1}. Bonds to OH are even stronger, with some dissociation energies approaching 134 kcal mol^{-1}. Finally, Al−F BDEs are by far the strongest, with values as high as 160 kcal mol^{-1}. These results are consistent with the fact that lower deposition

TABLE 2: Bond Additivity Corrections for the G2 Level of Theory (kcal mol^{-1})

species	bond length (no.), BAC								atomic correction	molecular correction
	Al−H	Al−Cl	Al−C	Al−O	Al−F	C−H	C−O	O−H		
$A1H_3$	1.589 (3), −0.11								−0.05	−1.72
AlH_2	1.600 (2), 0.03								−0.53	−0.86
AlH	1.659, 0.14								−1.02	−0.86
$AlCl_3$		2.069 (3), 1.49							−3.83	−1.72
$AlCl_2$ $^2A_1$		2.097 (2), 1.30							−3.05	−0.86
AlCl $^1\Sigma$		2.135, 1.08							−2.28	−0.86
AlF_3					1.645 (3), 2.84				−7.33	−1.72
AlF_2 $^2A'$					1.659 (2), 2.52				−5.38	−0.86
AlF $^1\Sigma$					1.671, 2.23				−3.44	−0.86
$Al(OH)_3$ C_3 axis				1.712 (3), 0.91				0.967 (3), 0.70	−1.55	−4.30
$Al(OH)_2$ $^2A_1$ planar, trans, trans				1.721 (2), 0.90				0.968 (2), 0.70	−1.53	−2.58
AlOH $^1A'$ linear				1.689, 1.01				0.959, 0.72	−1.52	−1.72
$Al(CH_3)_3$			1.969 (3), −0.18			1.096 (6), −0.14 1.094 (3), −0.14			6.11	−6.88
$Al(CH_3)_2$ $^2A'$			1.978 (2), −0.23			1.096 (4), −0.14 1.092 (2), −0.14			3.57	−4.30
$AlCH_3$ $^1A_1$			1.994, −0.28			1.098 (3), −0.14			1.04	−2.58
AlH_2Cl	1.579 (2), 0.12	2.097, 0.92							−1.31	−1.72
$AlHCl_2$	1.568, 0.36	2.081 (2), 1.21							−2.57	−1.72
HAlCl $^2A'$	1.600, 0.26	2.109, 1.03							−1.79	−0.86
AlH_2F	1.580 (2), 0.25				1.663, 1.99				−2.47	−1.72
$AlHF_2$	1.565, 0.62				1.653 (2), 2.42				−4.90	−1.72
HAlF	1.606, 0.38				1.667, 2.10				−2.96	−0.86
H_2AlOH	1.580, 0.03 1.589, 0.02			1.720, 0.61				0.968, 0.70	−0.55	−2.58
$HAl(OH)_2$ OAlOH cis, trans	1.577, 0.16			1.713, 0.77 1.718, 0.76				0.968, 0.70 0.967, 0.70	−1.05	−3.44
HAlOH $^2A'$ trans	1.601, 0.16			1.726, 0.74				0.968, 0.70	−1.03	−1.72
$AlH_2(CH_3)$ HCAlH planar	1.594 (2), 0.08		1.961, −0.58			1.092, −0.14 1.096 (2), −0.14			2.01	−3.44
$AlH(CH_3)_2$	1.600, 0.27		1.965 (2), −0.38			1.096 (4), −0.14 1.093 (2), −0.14			4.06	−5.16
$HAl(CH_3)$ $^2A'$ HAlCH trans	1.608, 0.22		1.973, −0.43			1.091, −0.14 1.096 (2), −0.14			1.52	−2.58
$AlFCl_2$		2.065 (2), 1.64			1.648, 2.56				−4.99	−1.72
AlF_2Cl		2.062, 1.78			1.646 (2), 2.70				−6.16	−1.72
ClAlF		2.097, 1.43			1.659, 2.39				−4.22	−0.86
$Al(OH)Cl_2$		2.070, 1.40 2.080, 1.36		1.701, 1.15				0.968, 0.70	−3.07	−2.58
$AlCl(OH)_2$ OAlOH cis, trans		2.082, 1.25		1.704, 1.04 1.708, 1.02				0.968, 0.70 0.967, 070	−2.31	−3.44
ClAlOH $^2A'$ trans		2.100, 1.19		1.717, 1.00				0.969, 0.70	−2.29	−1.72

TABLE 2: (Continued)

	bond length (no.), BAC								atomic correction	molecular correction
species	Al−H	Al−Cl	Al−C	Al−O	Al−F	C−H	C−O	O−H		
$AlCl_2(CH_3)$ HCAlCl planar		2.090 (2), 1.38	1.938, −0.11			1.092, −0.14 1.094 (2), −0.14			−0.52	−3.44
$AlCl(CH_3)_2$		2.115, 1.25	1.952 (2), −0.15			1.095 (4), −0.14 1.093 (2), −0.14			2.80	−5.16
$AlCl(CH_3)$ trans		2.118, 1.19	1.968, −0.20			1.095 (2), −0.14 1.092, −0.14			0.26	−2.58
$AlF_2(OH)$				1.699, 1.41	1.648, 2.59 1.653, 2.55			0.967, 0.70	−5.40	−2.58
$AlF(OH)_2$ FAlOH cis, cis				1.704 (2), 1.17	1.662, 2.27			0.966 (2), 0.70	−3.47	−3.44
FAlOH trans				1.718, 1.13	1.661, 2.28			0.968, 0.70	−3.46	−1.72
$Al(OH)_2CH_3$ OAlOH cis, trans			1.948, −0.30	1.718, 0.95 1.724, 0.94		1.094 (2), −0.14 1.093, −0.14		0.968, 0.70 0.966, 0.70	1.00	−5.16
$Al(OH)(CH_3)_2$			1.963, −0.24 1.955, −0.24	1.729, 0.98		1.094, −0.14 1.096, −0.14 1.095 (3), −0.14 1.093, −0.14		0.967, 0.70	3.56	−6.02
CH_3AlOH HOAlC cis			1.978, −0.29	1.730, 0.93		1.094 (2), −0.14 1.095, −0.14		0.969, 0.70	1.02	−3.44
HAl(OH)Cl ClAlOH cis	1.568, 0.27	2.095, 1.07		1.707, 0.89				0.968, 0.70	−1.81	−2.58
$HAl(CH_3)Cl$ HCAlCl trans	1.583, 0.32	2.105, 1.09	1.948, −0.34			1.093, −0.14 1.095 (2), −0.14			0.74	−3.44
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis	1.595, 0.22		1.950, −0.44	1.725, 0.80		1.095 (2), −0.14 1.093, −0.14		0.968, 0.70	1.50	−4.30
$Al(OH)CH_3Cl$		2.105, 1.23	1.939, −0.21	1.713, 1.07		1.094 (2), −0.14 1.092, −0.14		0.968, 0.70	0.24	−4.30
AlO $^2\Sigma$				1.648, 1.32					−2.00	−0.86
HAlO $^1\Sigma$	1.573, 0.18			1.629, 1.25					−1.52	−1.72
H_2AlO $^2B_2$	1.579 (2), 0.03			1.757, 0.66					−1.03	−1.72
AlC $^4\Sigma^-$			1.966, 0.00						−0.42	0.00
AlCH singlet linear			1.946, −0.09			1.089, 0.05			0.07	−1.72
HAlCH HAlCH trans $^2A''$	1.592, 0.23		1.882, −0.24			1.086, 0.05			0.55	−1.72
$HAlCH_2$ singlet linear C_{2v}	1.574, 0.24		1.795, −0.34			1.087 (2), −0.04			1.04	−2.58
H_2AlCH $^3A''$	1.586, 0.08 1.588, 0.08		1.896, −0.39			1.080, 0.05			1.04	−1.72
AlH_2OCH_3 HCOAl cis	1.589, 0.02 1.580, 0.03			1.714, 0.83		1.097, −0.15 1.094 (2), −0.15	1.418, −0.29		1.50	−4.30

temperatures are required when, for example, oxides are deposited by CVD from organoaluminum instead of halogenated compounds.[26,27]

These results indicate that bonds to aluminum are generally weaker than those to boron. For example, B−H bonds in trivalent boron compounds are on the order of 105 kcal mol^{-1}.[21] Bonds between aluminum and methyl groups are also significantly weaker than their boron counterparts, as discussed previously.[13] Dissociation of the first Al−CH_3 bond in trimethylaluminum is more than 20 kcal mol^{-1} weaker than the same bond in trimethylborane. Dissociation energies for bonds between boron and chlorine,[21] however, are very similar to those between aluminum and chlorine. Data for boron hydroxides are sparse, but heats of formation reported by Gurvich et al.[2] indicate that the analogous aluminum bonds are weaker as well. These comparisons are consistent with the general trends in main-group bond energies, which decrease as one proceeds down the periodic table from the first to the fourth row.[13]

TABLE 3: Calculated $\Delta H_f°(0\ K)$ and $\Sigma D_0(0\ K)$ for Selected Aluminum Compounds at Various Levels of Theory (kcal mol^{-1}), with Atomic Heats of Formation at 0 K

	$\Delta H_f°$(0K)					ΣD_0	
species	G2	BAC-QCI	BAC-G1	BAC-G2MP2	BAC-G2	BAC-G2	literature
AlH_3	30.4	36.4	31.1	32.4	32.5	200.6	200.8 ± 4.8,[a] 196.1,[c] 201.8 [d]
AlH_2	63.5	66.7	63.6	64.0	64.8	116.7	114.7 ± 4.8[a]
AlH	57.5	58.3	58.1	57.9	59.3	70.6	70.3 ± 0.4,[a] 66.9 ± 4.6,[b] 66.1,[c] 69.9,[d] 73.6,[e] 72.9 ± 0.2,[f] <70.6 [g]
$AlCl_3$	−142.2	−122.2	−138.0	−138.2	−141.1	305.1	303.4 ± 1.5 [a]
$AlCl_2\ ^2A_1$	−53.5	−38.7	−50.6	−51.2	−52.2	187.6	192.8 ± 9.6 [a]
$AlCl\ ^1\Sigma$	−14.0	−6.7	−12.0	−12.9	−12.0	118.8	119.1 ± 1,[a] 118.1, [g] 120.8 [k]
AlF_3	−286.8	−260.6	−284.2	−279.8	−286.3	419.9	421.8 ± 1.2,[a] 391.7,[c] 369.6 [d]
$AlF_2\ ^2A'$	−149.7	−129.8	−148.9	−145.1	−148.5	263.7	265.8 ± 7.2 [a]
$AlF\ ^1\Sigma$	−64.9	−55.1	−63.9	−62.0	−62.8	159.5	159.9 ± 1.2,[a] 160 ± 1.5,[b] 152.3,[c] 145.1,[d] 161.6,[e,k] 159 ± 3,[h] 160.4,[i] 162.5 [j]
$Al(OH)_3$ C_3 axis	−232.1	−215.3	−232.8	−228.7	−231.1	641.2	649.2 ± 12 [a]
$Al(OH)_2\ ^2A_1$ planar, trans, trans	−110.8	−97.1	−112.6	−109.2	−109.9	409.4	419.0 ± 12 [a]
$AlOH\ ^1A'$ linear	−44.0	−36.9	−44.2	−42.9	−42.5	231.4	234.3 ± 7.2 [a]
$Al(CH_3)_3$	−9.6	1.5	−8.3	−7.5	−7.0	1059.8	
$Al(CH_3)_2\ ^2A'$	37.9	45.1	38.6	38.8	39.9	688.1	
$AlCH_3\ ^1A_1$	43.0	45.9	43.7	43.7	45.2	357.9	
AlH_2Cl	−28.5	−18.2	−26.5	−25.9	−26.7	236.8	234.1 ± 7.2 [a]
$AlHCl_2$	−86.6	−71.4	−83.4	−83.3	−85.1	272.1	270.1 ± 7.2 [a]
$HAlCl\ ^2A'$	4.2	13.0	5.8	5.6	5.6	152.9	155.4 ± 7.2*a*
AlH_2F	−77.1	−64.4	−75.6	−73.6	−75.4	275.4	274.1 ± 7.2 [a]
$AlHF_2$	−184.3	−164.9	−182.2	−179.0	−183.2	350.0	348.5 ± 3.6 [a]
HalF	−43.8	−32.2	−43.4	−41.4	−42.5	190.8	191.4 ± 7.2 [a]
H_2AlOH	−57.4	−48.1	−57.1	−55.2	−55.7	347.8	
$HAl(OH)_2$ OAlOH cis, trans	−145.8	−132.6	−145.9	−142.9	−144.4	495.5	
$HAlOH\ ^2A'$ trans	−24.1	−16.2	−24.9	−23.3	−23.0	263.5	
$AlH_2(CH_3)$ HCAlH planar	17.3	24.9	18.3	19.2	19.5	486.9	
$AlH(CH_3)_2$	3.9	13.2	5.2	5.9	6.3	773.3	
$HAl(CH_3)\ ^2A'$ HAlCH trans	50.9	56.1	51.3	51.6	52.6	402.1	
$AlFCl_2$	−190.4	−168.5	−186.9	−185.4	−189.6	343.5	342.5 ± 1.9 [a]
AlF_2Cl	−238.7	−214.6	−235.7	−232.6	−238.0	381.8	381.9 ± 1.9 [a]
ClAlF	−101.5	−84.3	−99.6	−98.0	−100.2	225.5	229.3 ± 7.2,[a] 241 ± 15 [b]
$Al(OH)Cl_2$	−172.9	−154.3	−170.4	−169.1	−171.8	417.8	418.2 ± 12 [a]
$AlCl(OH)_2$ OAlOH cis, trans	−202.9	−185.2	−202.1	−199.3	−201.9	530.0	531.3 ± 12 [a]
$ClAlOH\ ^2A'$ trans	−82.5	−68.9	−82.0	−80.6	−81.4	298.8	305.9 ± 9.6 [a]
$AlCl_2(CH_3)$ HCAlCl planar	−102.3	−85.6	−98.8	−98.9	−100.5	560.8	
$AlCl(CH_3)_2$	−57.9	−44.3	−55.4	−55.1	−55.6	812.2	
$AlCl(CH_3)$ trans	−10.1	0.7	−8.4	−8.5	−8.4	440.1	
$AlF_2(OH)$	−269.3	−246.2	−267.9	−263.5	−268.6	494.4	497.1 ± 7.2 [a]
$AlF(OH)_2$ FAlOH cis, cis	−250.9	−230.4	−250.7	−246.3	−250.0	567.9	571.4 ± 12 [a]
FAlOH trans	−130.6	−114.1	−131.0	−127.5	−129.5	336.8	343.6 ± 12 [a]
$Al(OH)_2CH_3$ OAlOH cis, trans	−159.9	−145.5	−159.7	−157.0	−158.4	782.7	
$Al(OH)(CH_3)_2$	−85.4	−73.1	−84.2	−83.0	−83.3	921.9	
CH_3AlOH HOAlC cis	−36.6	−27.1	−36.8	−35.4	−35.1	548.8	
HAl(OH)Cl ClAlOH cis	−117.1	−103.2	−115.5	−114.0	−115.6	384.7	
$HAl(CH_3)Cl$ HCAlCl trans	−43.3	−31.2	−41.0	−40.6	−41.2	524.5	
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis	−71.7	−60.7	−70.9	−69.3	−69.7	635.1	
$Al(OH)CH_3Cl$	−132.2	−116.8	−130.4	−129.0	−130.5	672.8	
$AlO\ ^2\Sigma$	18.4	27.7	17.6	19.5	19.9	117.3	121.2 ± 1.2,[a] 121.2 ± 2,[b] 118.1 [e]
$HAlO\ ^1\Sigma$	−2.2	6.3	−1.8	−3.5	−0.4	189.3	187.7 ± 12 [a]
$H_2AlO\ ^2B_2$	11.30	20.95	12.05	14.15	13.33	227.2	
$AlC\ ^4\Sigma^-$	171.6	176.3	170.8	169.8	172.1	76.1	86 ± 12,[a] 78.6,[e] 76.1 [l]
AlCH singlet linear	156.7	162.4	157.2	157.1	158.4	141.4	
HAlCH HAlCH trans $^2A''$	124.5	135.1	125.2	129.5	125.7	225.8	
$HAlCH_2$ singlet linear C_{2v}	79.9	87.1	80.9	80.7	81.6	321.5	
$H_2AlCH\ ^3A''$	110.7	119.0	110.7	111.0	111.5	291.6	
AlH_2OCH_3 HCOAl cis	−47.5	−37.3	−46.0	−44.2	−44.9	610.3	
Al	78.23	78.23	78.23	78.23	79.73		
H	51.63	51.37	50.58	50.76	51.15		
Cl	28.59	29.87	30.35	30.03	29.37		
F	18.47	17.92	20.43	20.79	20.41		
O	58.99	56.91	59.31	59.77	59.49		
C	169.98	170.84	168.82	168.45	168.90		

[a] Reference 2. [b] Reference 1. [c] D_e, MP2 calculation. See ref 38. [d] D_e, QCI calculation. See ref 39. [e] CCSD(T)/WMR calculation. See ref 38. [f] Baltayan, P.; Nedelec, O. *J. Chem. Phys.* **1979**, *70*, 2399. [g] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand: New York, 1979. [h] Murad, E.; Hildenbrand, D. L.; Main, R. P. *J. Chem. Phys.* **1966**, *45*, 263. [i] D_e, MP4SDQ calculation: Peterson, K. A., Woods, R. C. *J. Chem. Phys.* **1988**, *89*, 4929. [j] MP4/6-311+G(MC)(3d2f) calculation. See ref 39. [k] G2 calculation, ref 40. [l] MRCI calculation. See ref 36.

Ligand substitution in trivalent aluminum compounds has very little effect on bond dissociation energies in these compounds. In general exchanging one ligand for another changes the BDE of the remaining ligands of that type by less than 1 kcal mol^{-1}. Increasing the number of halogen atoms in a molecule generally reduces the Al−halogen BDE, although the BDEs of the other ligands are not changed by more than ∼2 kcal mol^{-1}. These observations are consistent with the trends in heats of formation discussed above, again showing that bonding in these compounds is highly localized.

This localized behavior does not extend to nontrivalent compounds, however. In particular, the effect on the BDE of exchanging ligands in divalent species is much more profound. The unpaired electron in AlXY compounds is strongly affected

TABLE 4: ΔH_{f° (298 K) for the BAC-G2 Level of Theory with Error Estimates and Literature Values for Selected Aluminum Compounds (kcal mol^{-1})

species	ΔH_f^o	JANAF[b]	Gurvich[a]	other sources
AlH_3	30.9 ± 1.8		30.8 ± 4.8	26.9,[d] 24.2,[e] 13.6,[f] 84.5,[g] 30.6,[h] 29.5,[i] 29.1 [u]
AlH_2	64.1 ± 1.8		66.2 ± 4.8	51.8,[d] 50.4,[e] 45.4,[f] 10.7,[g] 61.8,[h] 62.4,[i] 63.5,[j] 63.4,[t] 63.1 [u]
AlH	59.2 ± 2.0	61.9 ± 4.8	59.6 ± 0.8	63.0,[d] 46.0,[e] 52.9,[f] 70.1,[g] 59.5,[h] 58.2,[i] 58.6,[t] 57.7 [u]
$AlCl_3$	−141.5 ± 4.4	−139.7 ± 0.7	−139.7 ± 1.2	−142.5,[c] −134.3,[k] −140 ± 0.43,[l] −149.2,[d] −140.3,[e] −140.3,[f] −122.1,[g] −126.8,[h] −146.3,[i] −139.4,[m] −146.4,[t] −139.8 [u]
$AlCl_2$ $^2A_1$	−52.4 ± 2.1	−66.9 ± 4.8	−57.6 ± 9.6	−71.4,[d] −74.6,[e] −74.0,[f] −68.2,[g] −46.8,[h] −57.4,[i] −57.3,[j] −79.1,[m] −57.4,[t] −51.8 [u]
AlCl $^1\Sigma$	−11.9 ± 1.3	−12.3 ± 1.5	−12.2 ± 0.7	−12.7,[d] −27.8,[e] −20.8,[f] −5.5,[g] −9.1,[h] −15.4,[i] −11.4,[m] −15.4,[t] −12.9 [u]
AlF_3	−287.1 ± 6.9	−289.0 ± 0.6	−289.0 ± 0.7	−287.6,[c] −291.9,[d] −291.3,[e] −285.8,[f] −291.5,[g] −287.9,[m] −290.4,[t] −286.2 [v]
AlF_2 $^2A'$	−148.9 ± 3.6	−166.1 ± 9.6	−151.0 ± 7.2	−152.4 [t]
AlF $^1\Sigma$	−62.8 ± 1.7	−63.5 ± 0.8	−63.1 ± 0.7	−65.7,[d] −83.6,[e] −77.9,[f] −50.1,[g] −61.7,[m] −65.4 [t]
$Al(OH)_3$ C_3 axis	−233.8 ± 3.1		−242.0 ± 12	
$Al(OH)_2$ $^2A_1$ planar, trans, trans.	−111.5 ± 2.9		−121.3 ± 12	
AlOH $^1A'$ linear	−42.8 ± 2.0	−43.0 ± 3.1	−46.1 ± 7.2	−34.5,[d] −61.1,[e] −40.1,[f] −33.4,[g] −40.0,[h] −45.5,[i] −44.7,[t] −43.8 [u]
$Al(CH_3)_3$	−12.8 ± 1.6			−19.4,[n] −20.5,[d] −40.1,[e] −27.5,[f] −5.7,[g] −17.8,[m] −20.9,[o] −5.6,[p] −13.1 [q]
$Al(CH_3)_2$ $^2A'$	36.2 ± 2.0			
$AlCH_3$ $^1A_1$	43.6 ± 2.4			
AlH_2Cl	−28.1 ± 1.3		−25.4 ± 7.2	−24.1[h], −30.7[i], −28.8[u]
$AlHCl_2$	−86.1 ± 2.7		−84.0 ± 7.2	−77.1[h], −89.8[i], −89.4[t], −85.6[u]
HAlCl $^2A'$	5.0 ± 1.0		2.5 ± 7.2	6.1[h], 1.5[i], 1.6[j], 4.7[u]
AlH_2F	−76.9 ± 2.1		−75.7 ± 7.2	
$AlHF_2$	−184.4 ± 4.4		−182.9 ± 3.6	
HAlF	−43.1 ± 1.8		−43.6 ± 7.2	
H_2AlOH	−57.9 ± 1.8			
$HAl(OH)_2$ OAlOH cis, trans	−146.9 ± 2.3			
HAlOH $^2A'$ trans	−24.3 ± 2.2			
$AlH_2(CH_3)$ HCAlH planar	16.4 ± 1.6			
$AlH(CH_3)_2$	1.7 ± 1.6			−6.4,[o] 6.2,[p] 0.9 [q]
$HAl(CH_3)$ $^2A'$ HAlCH trans	50.3 ± 1.9			
$AlFCl_2$	−190.1 ± 5.0	−189.0 ± 1.4	−189.1 ± 1.7	−195.4,[d] −191.4,[e] −186.7,[f] −178.0 [g]
AlF_2Cl	−238.7 ± 5.9	−238.8 ± 1.5	−238.8 ± 1.7	−243.0,[d] −241.6,[e] −236.2,[f] −234.6 [g]
ClAlF	−100.5 ± 2.5	−117.0 ± 15.1	−104.3 ± 7.2	−104.6 [t]
$Al(OH)Cl_2$	−173.0 ± 3.3		−173.3 ± 12	
$AlCl(OH)_2$ OAlOH cis, trans	−203.8 ± 2.8		−205.3 ± 12	
ClAlOH $^2A'$ trans	−82.3 ± 1.4		−89.3 ± 9.6	−86.0 [t]
$AlCl_2(CH_3)$ HCAlCl planar	−102.7 ± 2.6			−119.7 ± 1.7 [o]
$AlCl(CH_3)_2$	−59.6 ± 1.1			−79.9 ± 2.1 [o]
$AlCl(CH_3)$ trans	−10.3 ± 1.0			
$AlF_2(OH)$	−270.0 ± 5.2		−273.8 ± 9.6	
$AlF(OH)_2$ FAlOH cis, cis	−252.0 ± 3.9		−255.6 ± 12	
FAlOH trans	−130.5 ± 2.7		−137.2 ± 12	−133.5 [t]
$Al(OH)_2CH_3$ OAlOH cis, trans	−162.1 ± 2.1			
$Al(OH)(CH_3)_2$	−88.1 ± 1.4			
CH_3AlOH HOAlC cis	−37.8 ± 2.0			
HAl(OH)Cl ClAlOH cis	−117.4 ± 1.9			
$HAl(CH_3)Cl$ HCAlCl trans	−44.0 ± 1.2			
$HAl(OH)CH_3$ CAlOH trans,HCAlO cis	−73.3 ± 1.6			
$Al(OH)CH_3Cl$	−133.5 ± 1.8			
AlO $^2\Sigma$	19.9 ± 2.6	15.9 ± 1.9	16.1 ± 1.5	3.9,[d] −1.8,[e] 8.4,[f] 9.8,[g] 18.9,[h] 17.0,[i] 18.8,[j] 21.8,[m] 18.9,[t],18.8 [u]
HAlO $^1\Sigma$	−1.1 ± 3.5	8.0 ± 20.1	0.4 ± 12	189.9,[h] 189.9,[i] −5.3 [t]
H_2AlO $^2B_2$	11.9 ± 1.8			
AlC $^4\Sigma^-$	172.9 ± 2.8	164.8 ± 2.4	163.1 ± 12	172.5,[h] 171.5,[i] 171.7,[j] 172.8 [u]
AlCH singlet linear	158.6 ± 2.0			
HAlCH HAlCH trans $^2A''$	125.2 ± 4.0			
$HAlCH_2$ singlet linear C_{2v}	80.5 ± 1.6			
H_2AlCH $^3A''$	110.6 ± 1.4			
AlH_2OCH_3 HCOAl cis	−48.5 ± 1.6			
CH_3	34.77 ± 1.00	34.82 ± 0.19		35.06 ± 0.10 [r]
CH_2	93.63 ± 1.04	92.35 ± 1.00		
CH	141.18 ± 1.02	142.00 ± 4.18		
OH	9.23 ± 1.01	9.3 ± 0.29		8.89 ± 0.09 [s]
C	170.13 ± 1.10	171.29 ± 0.11		
O	59.93 ± 1.05	59.55 ± 0.02		
Cl	29.75 ± 1.55	28.99 ± 0.0019		
F	20.84 ± 1.07	18.98 ± 0.07		
H	51.59 ± 1.21	52.10 ± 0.0014		
Al	80.14 ± 2.35	78.80 ± 1.00	78.87 ± 0.72	

[a] Reference 2. [b] Reference 1. [c] G2, calculation uncorrected for atomic spin−orbit effects. See ref 7. [d] MNDO/d calculation. See ref 32. [e] MNDO calculation. See ref 32. [f] AM1 calculation. See ref 32. [g] PM3 calculation. See ref 32. [h] B3LYP calculation. See ref 11. [i] CBS-Q calculation. See ref 11. [j] CBS−RAD calculation. See ref 11. [k] K2−BVWN calculation. See ref 33. [l] Reference 28. [m] Reference 3. [n] Reference 29. [o] Reference 30. [p] B3LYP/6-311++G(2df,pd) calculation. See: Simka, H.; Willis, B. G.; Lengyel, I.; Jensen, K. F. *Prog. Crystal Growth Charact.* **1997**, *35*, 117. Willis, B. G.; Jensen, K. F. *J. Phys. Chem. A* **1998**, *102*, 2613. [q] G2MP2 calculation. See footnote *p*. [r] Dobis, O.; Benson, S. W. *Int. J. Chem. Kinet.* **1987**, *19*, 691. [s] Rusic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A* **2001**, *105*, 1. [t] Reference 41. [u] Spin−orbit-corrected G2 calculation. See ref 11. [v] Spin−orbit-corrected G2 calculation. See ref 10.

by the electronegativity of the ligands. If electronegativities of the exchanged ligands are substantially different, e.g., when replacing H or CH_3 by Cl, F, or OH, a considerable redistribution of the electron density occurs, with the unpaired electron going to the more electronegative atom. This makes the bond to the electronegative ligand much stronger than the bond to

TABLE 5: Thermochemistry Parameters at Various Temperatures (K)

	$\Delta H_f^{o\,a}$	$S^{\circ\,b}$	$\Delta G_f^{o\,a}$					
species	298 K	298 K	300 K	600 K	1000 K	1500 K	2000 K	2500 K
AlH_3	30.9	49.7	27.3	15.1	36.9	42.4	48.0	53.6
AlH_2	64.1	51.1	55.4	38.0	52.8	49.8	47.2	44.8
AlH	59.2	44.9	47.7	27.4	38.1	30.1	22.5	15.2
$AlCl_3$	−141.5	75.4	−142.9	−153.4	−130.0	−122.5	−114.8	−107.1
$AlCl_2\ ^2A_1$	−52.4	69.4	−60.0	−76.5	−60.8	−62.8	−64.2	−65.5
$AlCl\ \mathbf{^1\Sigma}$	−11.9	54.6	−23.0	−43.1	−32.0	−39.6	−46.6	−53.3
AlF_3	−287.1	66.6	−288.0	−297.9	−273.4	−264.7	−255.7	−246.6
$AlF_2\ ^2A'$	−148.9	63.4	−156.1	−172.2	−155.9	−156.9	−157.5	−157.9
$AlF\ ^1\Sigma$	−62.8	51.4	−73.7	−93.5	−82.0	−89.1	−95.6	−101.8
$Al(OH)_{\mathbf{3}}\ \mathbf{C}_3$ axis	−233.8	74.0	−222.8	−220.7	−180.6	−152.6	−125.9	−99.7
$Al(OH)_2\ ^2A_1$ planar, trans, trans	−111.5	68.1	−110.6	−118.6	−91.7	−80.3	−69.0	−57.9
$AlOH\ ^1A'$ linear	−42.8	49.6	−48.4	−62.8	−44.3	−42.4	−40.0	−37.4
$Al(CH_3)_3$	−12.8	94.6	−0.7	2.6	45.9	78.4	110.2	140.9
$Al(CH_3)_2\ ^2A'$	36.2	80.1	38.3	31.6	61.3	77.0	92.6	107.6
$AlCH_3\ ^1A_1$	43.6	57.2	38.1	24.2	44.0	47.6	51.6	55.7
AlH_2Cl	−28.1	60.7	−31.7	−44.1	−22.7	−17.7	−12.5	−7.4
$AlHCl_2$	−86.1	69.3	−89.0	−100.7	−78.8	−73.2	−67.3	−61.5
$HAlCl\ ^2A'$	5.0	61.8	−3.6	−21.0	−6.4	−9.6	−12.4	−15.0
AlH_2F	−76.9	57.7	−80.3	−92.4	−70.6	−65.1	−59.5	−53.8
$AlHF_2$	−184.4	63.4	−186.9	−198.2	−175.6	−169.0	−162.3	−155.5
HAlF	−43.1	58.8	−51.5	−68.7	−53.8	−56.5	−58.9	−61.0
H_2AlOH	−57.9	60.9	−57.5	−65.9	−39.2	−27.7	−16.2	−5.1
$HAl(OH)_2$ OAlOH cis, trans	−146.9	68.7	−141.6	−145.1	−112.2	−93.2	−74.6	−56.6
$HAlOH\ ^2A'$ trans	−24.3	60.7	−28.6	−41.6	−21.2	−17.2	−13.2	−9.3
$AlH_2(CH_3)$ HCAlH planar	16.4	69.0	16.7	8.4	35.7	48.0	60.3	72.2
$AlH(CH_3)_2$	1.7	81.4	8.1	5.7	41.2	63.8	86.1	107.6
$HAl(CH_3)\ ^2A'$ HAlCH trans	50.3	65.3	47.0	35.1	57.5	64.0	70.6	77.1
$AlFCl_2$	−190.1	74.7	−192.0	−202.9	−180.1	−173.3	−166.3	−159.3
AlF_2Cl	−238.7	71.7	−240.4	−251.1	−227.9	−220.7	−213.3	−205.8
ClAlF	−100.5	67.8	−108.3	−125.0	−109.6	−111.8	−113.6	−115.1
$Al(OH)Cl_2$	−173.0	78.2	−171.2	−178.5	−150.8	−138.2	−125.8	−113.6
$AlCl(OH)_2$ OAlOH cis, trans	−203.8	77.3	−197.8	−200.7	−167.3	−147.7	−128.7	−110.1
$ClAlOH\ ^2A'$ trans	−82.3	70.0	−86.1	−98.8	−78.0	−73.9	−69.6	−65.3
$AlCl_2(CH_3)$ HCAlCl planar	−102.7	86.2	−101.0	−108.2	−79.9	−66.2	−52.6	−39.4
$AlCl(CH_3)_2$	−59.6	89.0	−52.2	−53.7	−17.3	6.5	30.0	52.7
$AlCl(CH_3)$ trans	−10.3	74.8	−13.1	−24.8	−2.1	4.8	11.8	18.7
$AlF_2(OH)$	−270.0	72.3	−267.9	−274.7	−246.3	−233.0	−219.8	−206.7
$AlF(OH)_2$ FAlOH cis, cis	−252.0	74.7	−245.9	−248.7	−214.9	−195.5	−176.4	−157.5
FAlOH trans	−130.5	67.0	−134.1	−146.5	−125.4	−120.7	−115.9	−111.1
$Al(OH)_2CH_3$ OAlOH cis, trans	−162.1	84.4	−151.8	−150.4	−110.6	−83.0	−56.1	−30.1
$Al(OH)(CH_3)_2$	−88.1	89.6	−76.9	−74.4	−32.9	−3.1	26.1	54.4
CH_3AlOH HOAlC cis	−37.8	77.2	−37.3	−45.6	−18.6	−6.5	5.4	16.9
HAl(OH)Cl ClAlOH cis	−117.4	69.5	−116.3	−124.1	−97.0	−85.0	−73.0	−61.0
$HAl(CH_3)Cl$ HCAlCl trans	−44.0	76.7	−42.7	−50.2	−22.0	−8.5	4.9	18.0
$HAl(OH)CH_3$ CAlOH trans, HCAl cis	−73.3	74.2	−67.2	−69.9	−35.4	−14.3	6.7	27.2
$Al(OH)CH_3Cl$	−133.5	82.9	−126.7	−128.9	−93.8	−72.0	−50.4	−29.6
$AlO\ ^2\Sigma$	19.9	52.4	8.8	−11.2	−0.2	−7.9	−15.1	−22.0
$HAlO\ ^1\Sigma$	−1.1	52.9	−7.7	−23.1	−6.0	−6.3	−6.4	−6.4
$H_2AlO\ ^2B_2$	11.9	59.26	8.1	−4.5	16.5	20.9	25.5	30.1
$AlC\ ^4\Sigma^-$	172.9	54.0	154.4	126.8	127.8	107.8	88.6	69.8
AlCH singlet linear	158.6	40.5	148.8	130.1	143.0	138.0	133.8	129.9
HAlCH HAlCH trans $^2A''$	125.2	61.0	114.0	93.9	104.7	96.6	88.9	81.3
$HAlCH_2$ singlet linear C_{2v}	80.5	61.8	73.6	58.1	75.4	75.5	76.0	76.4
$H_2AlCH\ ^3A''$	110.6	65.9	102.5	85.5	100.6	97.8	95.1	92.3
AlH_2OCH_3 HCOAl cis	−48.5	72.1	−41.8	−43.5	−7.5	15.7	38.6	60.7

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1}.

the more electropositive ligand. This effect can be clearly seen in Table 6. For example, when substituting F for H in AlH_2 to form HAlF, the Al−H BDE drops from 46.7 to 31.9 kcal mol^{-1}. In contrast, substitution of CH_3 for H in AlH_2 decreases the Al−H BDE by less than 2 kcal mol^{-1}.

Successive removal of ligands within a given molecule results in a high−low−high trend in BDEs that is displayed by silicon compounds (see for example ref 19) as well as other group III compounds.[21] For example, the Al−Cl BDEs in $AlCl_3$, $AlCl_2$, and AlCl, are 118.1, 69.5, and 119.7 kcal mol^{-1}, respectively. This trend is evident for all five ligands examined in this study. The stronger bond in AlX_3 relative to AlX_2 species is a consequence of the energy penalty paid for unpairing electrons, resulting in a product with a doublet ground state. Alternatively, breaking the Al−X bond in AlX_2 requires less energy, since there is a thermodynamic advantage to pairing the valence electrons on aluminum (all AlX species have ^1S ground states).

B. Comparisons with Experimental Data. The BAC-G2 heats of formation for the aluminum hydrides, fluorides, and chlorides are generally in good agreement with the primary critical reviews of thermodynamic data, Gurvich et al.,[2] and the JANAF Tables.[1] In particular, the BAC-G2 value is in good agreement with the data in these reviews, as well as other sources,[3,28] for $AlCl_3$ and AlF_3. This is encouraging, since the experimental data for these compounds are probably the most accurate of those available for aluminum-containing species.

TABLE 6: Calculated Bond Dissociation Enthalpies (BDE) at 298 K for Selected Aluminum Compounds (kcal mol^{-1})

	BDE					
species	Al−H	Al−C	Al−O	Al−Cl	Al−F	C−O
AlH_3	84.8					
AlH_2	46.7					
AlH	72.5					
$AlCl_3$				118.9		
$AlCl_2$ $^2A_1$				70.3		
AlCl $^1\Sigma$				121.8		
AlF_3					159.0	
AlF_2 $^2A'$					106.9	
AlF $^1\Sigma$					163.8	
$Al(OH)_3$ C_3 axis			131.5			
$Al(OH)_2$ $^2A_1$ planar, trans, trans			77.9			
AlOH $^1A'$ linear			132.2			
$Al(CH_3)_3$		83.8				
$Al(CH_3)_2$ $^2A'$		42.2				
$AlCH_3$ $^1A_1$		71.3				
AlH_2Cl	84.7			122.0		
$AlHCl_2$	85.3			120.9		
HAlCl $^2A'$	34.7			84.0		
AlH_2F	85.4				161.8	
$AlHF_2$	87.1				162.1	
HAlF	31.9				123.1	
H_2AlOH	85.2		131.2			
$HAl(OH)_2$ OAlOH cis, trans	87.0		131.8			
HAlOH $^2A'$ trans	33.1		92.7			
$AlH_2(CH_3)$ HCAlH planar	85.5	82.5				
$AlH(CH_3)_2$	86.1	83.4				
$HAl(CH_3)$ $^2A'$ HAlCH trans	44.9	43.7				
$AlFCl_2$				119.4	158.5	
AlF_2Cl				119.6	159.0	
ClAlF				67.5	109.4	
$Al(OH)Cl_2$			129.8	120.5		
$AlCl(OH)_2$ OAlOH cis, trans			130.7	122.1		
ClAlOH $^2A'$ trans			79.6	69.3		
$AlCl_2(CH_3)$ HCAlCl planar		85.1		122.2		
$AlCl(CH_3)_2$		84.1		125.6		
$AlCl(CH_3)$ trans		33.2		83.7		
$AlF_2(OH)$			130.3		160.3	
$AlF(OH)_2$ FAlOH cis, cis			130.7		161.3	
FAlOH trans			76.9		108.5	
$Al(OH)_2CH_3$ OAlOH cis, trans		85.4	133.5			
$Al(OH)(CH_3)_2$		85.1	133.5			
CH_3AlOH HOAlC cis		29.8	90.6			
HAl(OH)Cl ClAlOH cis	86.7		131.6	122.9		
$HAl(CH_3)Cl$ HCAlCl trans	85.3	83.8		124.1		
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis	87.1	83.8	132.8			
$Al(OH)CH_3Cl$		86.0	132.4	125.5		
AlO $^2\Sigma$			120.2			
HAlO $^1\Sigma$	72.6		120.2			
H_2AlO $^2B_2$	38.6		112.1			
AlC $^4\Sigma^-$		77.4				
AlCH singlet linear		62.7				
HAlCH HAlCH trans $^2A''$	85.0	75.2				
$HAlCH_2$ singlet linear C_{2v}		72.3				
H_2AlCH $^3A''$	66.2	94.7				
AlH_2OCH_3 HCOAl cis						95.2

The biggest disagreements occur for the divalent species, whose heats of formation in the critical reviews were obtained through estimation techniques. The agreement is particularly poor with the JANAF heats of formation (differences as large as 15 kcal mol^{-1} for $AlCl_2$) and indicates that the JANAF values are likely in error. Data for AlH_3 and $AlCl_2$ from the older NBS Tables[3] also do not agree well with the BAC-G2 values. The estimated values reported by Gurvich et al. for the divalent species are in much better agreement with the BAC-G2 values. Predicted values for the diatomics AlH, AlF, and AlCl are in quite good agreement with the standard sources. Values for mixed halide/hydride species (i.e., AlH_nX_{3-n}, X = F, Cl; $n = 1-3$) estimated by Gurvich et al. for the most part agree well with theory. This is not surprising, since the linear estimations used by those authors are consistent with the observation (discussed earlier) that bonding in these compounds appears to be quite localized.

Unfortunately, data for organometallic aluminum compounds are quite thin, although several sources report a heat of formation for trimethylaluminum.[3,29,30] The value in the NBS Tables (−17.8 kcal mol^{-1})[3] and the value preferred by Cox and Pilcher (−20.9 ± 1.7 kcal mol^{-1})[4] are significantly lower than the BAC-G2 value of −12.8 kcal mol^{-1}. Cox and Pilcher list an alternate measurement obtained by Long and Norrish[31] (−13.6 ± 2.5 kcal mol^{-1}) that is actually in better agreement with the calculation. A more recent compilation by Pilcher and Skinner[29] gives −19.4 kcal mol^{-1}. An estimated heat of formation for $AlH(CH_3)_2$ reported by Smith (−6.4 kcal mol^{-1}) does not agree well with the BAC-G2 value.[30] Thus, none of the reported values

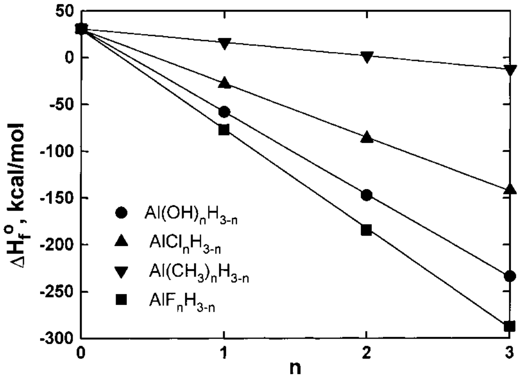

Figure 1. BAC-G2 heats of formation for substitution of H by R in the series AlH_3R_{3-n}, R = OH, F, Cl, CH_3.

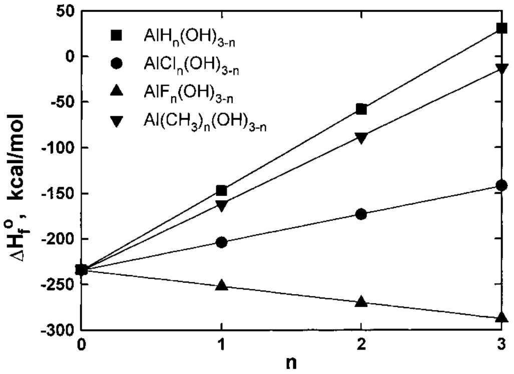

Figure 2. AC-G2 heats of formation for OH substitution in the series $AlR_3(OH)_{3-n}$, R = H, CH_3, F, Cl.

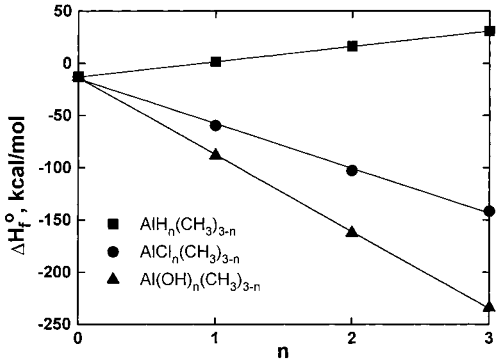

Figure 3. BAC-G2 heats of formation for substitution of CH_3 by R in the series $AlR_3(CH_3)_{3-n}$, R = H, Cl, OH.

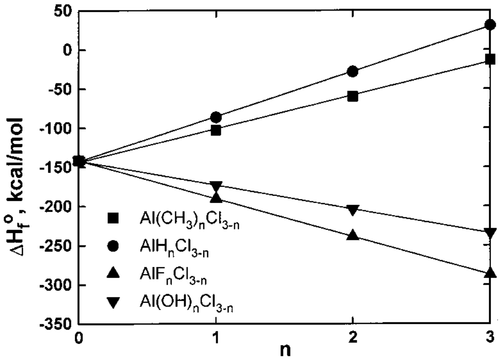

Figure 4. BAC-G2 heats of formation for chlorine substitution in the series AlR_3Cl_{3-n}, R = H, OH, F, CH_3.

is in particularly good agreement with the BAC-G2 prediction, suggesting that additional experimental and theoretical investigations should be performed to add confidence to the theoretical result.

Data for oxygen-containing aluminum compounds are also rare, making it difficult to validate model predictions. The diatomic molecule AlO is the only species that can be considered well-characterized. Heats of formation for AlO in both JANAF and Gurvich et al. are lower than the BAC-G2 prediction by about 4 kcal mol^{-1}. The only trivalent compound with a reported heat of formation is $Al(OH)_3$, for which the Gurvich et al. report an estimated value of −242 kcal mol^{-1}, and the NBS Tables report −305 kcal mol^{-1}.[3] Both values are in serious disagreement with the BAC-G2 prediction of −233.8 kcal mol^{-1}. Estimated heats of formation given by Gurvich et al. for $Al(OH)_2$ and AlOH also do not agree well with the theory (Table 4). The JANAF Tables report a heat of formation for HAlO nearly 9 kcal mol^{-1} higher than the BAC-G2 prediction. The estimation techniques employed by Gurvich et al. and JANAF involved average bond energies in various aluminum compounds (including halides as well as oxygen-containing compounds), so it is not surprising that a substantial error could result. As in the case of the organometallic compounds, additional experimental data are required to fully validate the computational predictions for aluminum−oxygen compounds, although it seems likely that the data in the NBS Tables for $Al(OH)_3$ are in error.

C. Comparisons with Other Quantum-Chemistry Predictions. Although it is not the purpose of this article to perform a comprehensive review of theoretical treatments of aluminum compounds, it is enlightening to compare the results of selected methods that have been published with the predictions of the BAC-G2 method. Heats of formation for aluminum-containing compounds obtained from quantum-chemistry techniques are more numerous than experimental data. Methods including semiempirical techniques,[32] density functional theory (DFT),[11,33−35] and high-level calculations[6,7,11,13,33,34,36−41] have been employed, although none of these studies treats as large a set of molecules as are examined here.

We will not discuss the uncorrected G2 results (Table 3) further, since these have already been discussed here and by other investigators.[6,7,11,42] However, we remark that G2 predictions for aluminum halides that are both corrected[10,11] and uncorrected[7] for atomic spin−orbit energies exist in the literature, which can lead to some confusion regarding the accuracy of this method. The BAC-G2 method does not explicitly correct for the atomic spin−orbit interaction (which would be accomplished by adding experimental spin−orbit interaction energies to the raw G2 atomic energies used in the calculation of the heat of atomization, ΣD_0). Instead, the BAC-G2 atomic corrections implicitly account for spin−orbit interactions that may exist. It is worth noting that, while applying atomic spin−orbit corrections improves the agreement between the G2 prediction and experiment for $AlCl_3$, this actually makes the agreement worse for AlF_3.[10] This reflects the fact that errors in G2 heats of formation for halogenated species are not purely caused by the lack of spin−orbit corrections but are also due to factors such as basis-set superposition errors, which are evidently more serious in compounds of fluorine than of chlorine.

The most comprehensive investigations prior to this one in which a high-level quantum-chemistry method was applied to a series of aluminum compounds are those of Swihart and Catoire (SC)[11] and Politzer et al.,[41] each of whom examined a series of compounds expected to be present during combustion of aluminum to form particles. SC used two complete basis set methods (CBS-Q and CBS-RAD) as well as DFT (discussed below). Politzer et al. used CBS-QB3 calculations exclusively. In both cases, the CBS methods are generally in agreement with both experiment and the BAC-G2 predictions, but the predicted heats of formation are almost uniformly more negative than both. The poor performance with regard to chlorides is also noteworthy; this has already been remarked on with regard to polychlorides in general.[10] The only instance in which the CBS prediction is more positive than the BAC-G2 value is the heat of formation reported by SC for HAlO. In this case, the value of 189.9 kcal mol^{-1} differs considerably from the BAC-G2 value (-1.1 kcal mol^{-1}). Personal communication with the authors of ref 11 indicates that this disagreement is due to an error in converting the G2 results to a heat of formation; the correct G2 heat of formation at 298 K for HAlO should be -3.69 kcal mol^{-1}, which is in agreement with the BAC-G2 value but is again more negative.[43]

Another example of an application of a composite method to the prediction of aluminum thermochemistry is that of Curtiss et al., who used the G3 method[9] (which corrects some of the deficiencies of the G2 method) to predict heats of formation for AlF_3 and $AlCl_3$. The G3 prediction for AlF_3 is in somewhat better agreement with the value in the JANAF Tables (1.1 kcal mol^{-1} deviation for G3 vs -1.4 kcal mol^{-1} for G2), but the agreement is actually worse for $AlCl_3$, being 3.3 kcal mol^{-1} higher than the experimental value.

SC also report heats of formation obtained from DFT(B3LYP) calculations, and there is one application of a relatively new DFT variant, K2-BVWN, to $AlCl_3$. In all cases, the predictions of the DFT methods are high relative to both experiment and the BAC-G2 results, in some cases by large amounts. Predicted values for the hydrides are in generally good agreement with experiment, although in this case the prediction for AlH_2 is somewhat low with respect to the estimation of Gurvich et al., but within the estimated uncertainty. Agreement with the experimental values of the chlorides is poor in all three cases. For example, the DFT(B3LYP) prediction for $AlCl_3$ is too high by 13 kcal mol^{-1}. The K2-BVWN method is somewhat better, but is still >5 kcal mol^{-1} higher than the experimental value.

As might be expected, the accuracy of the semiempirical approaches is poorer than that of the higher-level calculations, although this is not uniformly true. For example, in a recent paper, Thiel and Voityuk[32] described predictions for a small set of aluminum compounds obtained from AM1, PM3, MNDO, and a modified version of MDNO they developed that includes d orbitals (MNDO/d). Although most of these methods are reasonably accurate for closed-shell systems, errors can be high for both closed- and open-shell species. For example, MNDO/d predicts -149.2 kcal mol^{-1} for the heat of formation of $AlCl_3$, which is nearly 10 kcal mol^{-1} more negative than the established experimental result published by Gurvich et al. and in the JANAF Tables. With the exception of MNDO/d, the semiempirical methods disagree with the established heat of formation for AlCl by at least 6.5 kcal mol^{-1}. Although heats of formation for organometallic compounds are not as well established, the semiempirical predictions for $Al(CH_3)_3$ cover a range spanning nearly 35 kcal mol^{-1}. It would thus appear that these methods, despite their computational efficiency, are not sufficiently accurate to provide thermochemical data for modeling purposes.

IV. Summary and Conclusions

Thermodynamic data, in the form of heats of formation, entropies, and heat capacities, have been obtained from BAC-G2 predictions for a large set of aluminum compounds. In those cases where accurate experimental heats of formation are available (primarily halides), the BAC-G2 heat of formation is generally within 2 kcal mol^{-1} of the value reported in critical reviews. The good agreement between theory and experiment is particularly encouraging for compounds such as $AlCl_3$ that contain more than one halogen atom; the values predicted by G2 and other composite methods such as CBS and G3 deviate from experiment by ≥ 3 kcal mol^{-1} for$AlCl_3$. Predictions for organometallic compounds, though not firmly validated due to the lack of experimental data, appear well-behaved. Similarly, data for hydroxides and other oxygen-containing species are likely to be more accurate than either the limited experimental data available or the estimated values obtained from linear approximation methods.

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Supporting Information Available: Tables of atomic coordinates, moments of inertia, vibrational frequencies, electronic energies, and polynomial coefficients for thermochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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