Computational Study of the Enthalpies of Formation, $\Delta_f H°$, and Mean Bond Enthalpies, mBEs, of $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F−I)

Ines Raabe, Daniel Himmel, and Ingo Krossing*

Albert-Ludwigs-Universität Freiburg, Institut für Anorganische und Analytische Chemie, Albertstr. 21, D-79104 Freiburg i. Br., Germany

To compensate for lacking experimental standard enthalpies of formation $\Delta_f H°$ of haloboranes/−boranates as well as the isoelectronic halocarbenium ions and halomethanes, high-level quantum chemical calculations up to the ccsd(t)/(SDB-)aug-cc-pVQZ level have been performed to establish these values. Very reliable experimental data (e.g., $\Delta_f H°$ of HCl, F, and CH_4) or at the G3 level established values (e.g., $\Delta_f H°$ of CF_3^+ = 410 kJ mol^{-1}) were used as anchor points to obtain accurate absolute $\Delta_f H°$ and mean bond enthalpy (mBE) values. To further minimize systematic errors of the protocol, all derived quantities were assessed in isodesmic reactions at the G3 and ccsd(t) level using the (SDB-)aug-cc-PVTZ basis set. The obtained $\Delta_f H°$ values are in very good agreement to (scarcely available) accurate experimental and computational data. Almost all B-containing compounds have been assessed for the first time. We derived "best" $\Delta_f H°$ values and used them to determine the mean E−X bond enthalpies in $H_{4-n}EX_n^{-/0}$ and $H_{3-n}EX_n^{0/+}$ (with n = 1−3, E = B, C, and X = F−I). In each of the series, the $\Delta_f H°$ values increase from fluorine to iodine, and except for the iodine-containing carbenium ions and the bromo- and iodomethanes, the $\Delta_f H°$ values become lower with the more halogen atoms that are present in the particle. The boron containing species always have a lower $\Delta_f H°$ than the isoelectronic carbenium ions and methanes, and the $H_{4-n}EX_n^{-/0}$ are lower in energy than the parent $H_{3-n}EX_n^{+/0}$. This reflects the greater average B−X bond strengths.

1. Introduction

Haloboranes and halomethyl cations are isoelectronic. However, while haloboranes are long known and in large scale technically employed Lewis acids,[1] the halomethyl cations are a more recent addition that are only in part accessible in condensed phases[2−5] but readily accessible in the gas phase (mass spectrometry).[6,7] Earlier studies[2−4,8] agree on different reactivities and bonding: In the halomethyl cations, the positive charge is delocalized over the halogen atoms, leading to partial π bonding contributions. However, the amount of π bonding present in haloboranes is under debate. In order to find out more about the bonding in these species, an important input would be systematically derived mean bond enthalpies (mBEs) of the E−X bonds (E = B, C) in compounds that formally have and do not have the possibility to π backbond. A direct access to the mBEs is the use of the enthalpies of formations $\Delta_f H°$ of the species in question. Therefore, we establish in this paper accurate $\Delta_f H°$ values and E−X mBE values of the species collected in Figure 1.
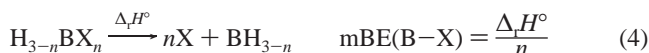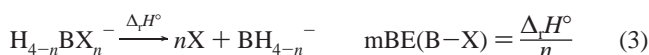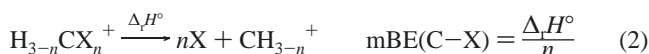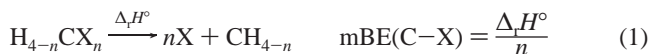
However, only for the minority of compounds shown in Figure 1 as well as the small particles further needed to assign mBEs, reliable experimental $\Delta_f H°$ values are known. Especially for some small and reactive species formed upon the E−X bond cleavage reactions but also for some of the halocalocarbenium ions or halomethanes (e.g., CF_3^+, H_2CBr_2, HCX_3 with X = Br, I), no accurate data are available. The same holds for the haloboranes and the haloborate anions. For the bromine- and iodine-containing halomethanes, calculated $\Delta_f H°$ values (at the QCISD(T)/6-311+G(3df,2p) level have been published two years ago.[9] We decided also to re-determine these values to

have a cross-check for our methods and because we wanted to use the same methodology for all particles as only this approach allows for maximum error cancellation and internal consistency.

2. Methodology and Results

2.1. Overview and Strategy. Flow-charts to establish the desired $\Delta_f H°$ values are delineated in Schemes 1 and 2. Based on these equations, the $\Delta_f H°$ values were assessed in isodesmic reactions using either G3 (for F and Cl containing species) or ccsd(t)/aug-cc-pVTZ (for Br and I containing species). As a control, MP2/TZVPP was also used. ZPEs and thermal contributions to the enthalpies were included at the unscaled (RI-)BP86/SV(P) level, which usually gives scaling factors close to unity. Experimental data were taken from the NIST database and are referenced with their original publications. All $\Delta_f H°$ values given in this study are gas-phase values at 298.15 K.

Once the $\Delta_f H°$ values are established properly, they are used to calculate the mean E−X (E = B, C) bond energies, mBEs, in these species through the following homolytic bond cleavage reactions (eqs 1−4):

$$H_{4-n}CX_n \xrightarrow{\Delta_r H°} nX + CH_{4-n} \qquad mBE(C-X) = \frac{\Delta_r H°}{n} \qquad (1)$$

$$H_{3-n}CX_n^+ \xrightarrow{\Delta_r H°} nX + CH_{3-n}^+ \qquad mBE(C-X) = \frac{\Delta_r H°}{n} \qquad (2)$$

$$H_{4-n}BX_n^- \xrightarrow{\Delta_r H°} nX + BH_{4-n}^- \qquad mBE(B-X) = \frac{\Delta_r H°}{n} \qquad (3)$$

$$H_{3-n}BX_n \xrightarrow{\Delta_r H°} nX + BH_{3-n} \qquad mBE(B-X) = \frac{\Delta_r H°}{n} \qquad (4)$$

For all equations, n ranges from 1 to 3. Thus, the $\Delta_f H°$ values of the small particles X, CH_{4-n}, CH_{3-n}^+, BH_{4-n}^-, and BH_{3-n}

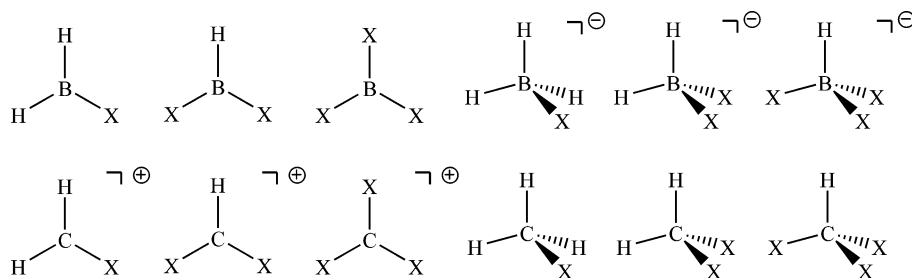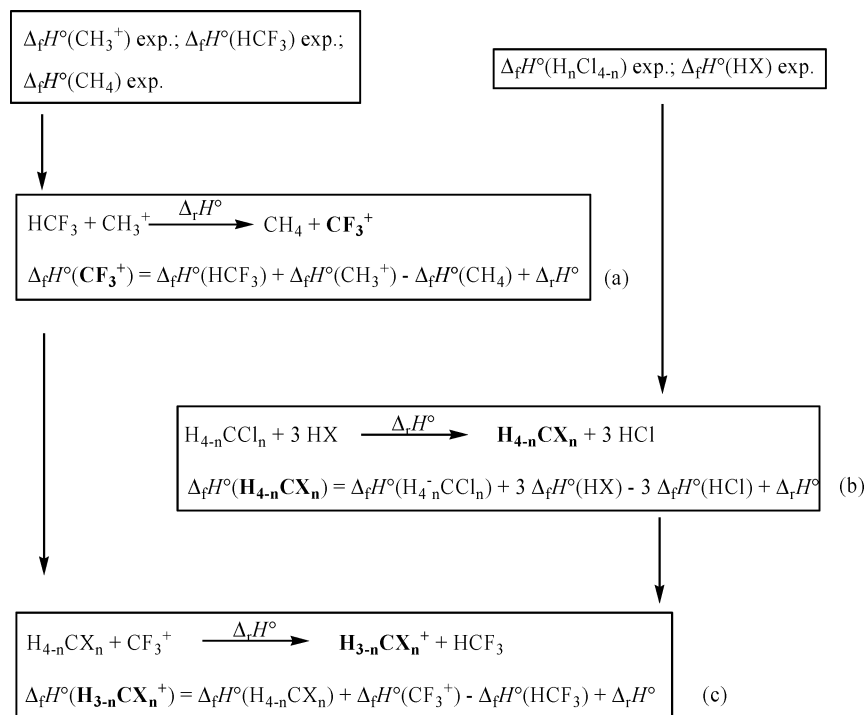* Corresponding author. Phone: +49 761 203 6122. E-mail: krossing@uni-freiburg.de.

Figure 1. Overview of the species investigated in this study (X = F−I).

SCHEME 1: Strategy to Obtain $\Delta_f H°$ of Halomethanes and Halomethyl Cations

are needed. They were either taken from reliable experimental data or calculated using the G3 method.

2.2. Choice of the Quantum Chemical Method. Before starting the calculations of $\Delta_f H°$ values, one has to choose the most appropriate quantum chemical method for each system and also the "best" reaction equation. In the ideal case, these reactions are isodesmic, which means that the number and the type of bonds both of starting materials and products are equal, so that error cancellation is maximal. However, highly accurate methods have to be used if possible.

To find out which method is the best compromise between accuracy and computing time, the electronically demanding homolytic cleavage of the F_2 molecule has been chosen as a test reaction for the method and basis set dependence. In Table 1, the results of these calculations obtained with different methods and basis sets are collected.

For both reactions, the ccsd(t)/aug-cc-pVDZ value lies far away from the data obtained by larger basis sets or by the G3 method. The average value from ccsd(t)/CBS and G3 (153 kJ mol^{-1}) differs only by 6 kJ mol^{-1} from the experimental value (159 kJ mol^{-1}),[11] indicating that the quantum chemical methods used in this study are even suitable to describe such electronically delicate and problematic reactions.

As a second test system, the CF_3^+ cation has been chosen. For the $\Delta_f H°$ of this cation, the available experimental data range from 359 to 449 kJ mol^{-1}, depending on the method used to determine the $\Delta_f H°$[11,12] (see Table 2).

This underlines the difficulties coming along with the experimental measurements. The value for $\Delta_f H°$ of CF_3^+ obtained by the G3 calculations (409.6 kJ/mol, from eq a in Scheme 1) lies in the midst of the experimentally measured data and is in very good agreement with the experimental value that appears to be most accurate (407.5 ± 4 kJ mol^{-1})[13]. The value is also in good agreement with high level calculations performed by Dixon et al. that gave $\Delta_f H(0 \text{ K})$ of CF_3^+ as 410 kJ mol^{-1} (98.0 ± 1.2 kcal mol^{-1}).[20]

Since it appeared that G3 is a suitable method both concerning accuracy and computing time, all quantities derived for species not containing Br or I were calculated using this method. For species containing heavier atoms, G3 is not applicable, and therefore, the ccsd(t) level of theory in combination with an isodesmic reaction for error cancellation was chosen. Therefore, all Br and I containing particles have been optimized with the ccsd(t)/(SDB-)aug-cc-pVTZ method. The calculated structural parameters of all $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F−I) are collected in Table 3.

Generally, the agreement between calculation and available experiment is very good. This good agreement of the structural parameters further supports the conclusions drawn from the calculations of the energetics of the indicated compounds. Many
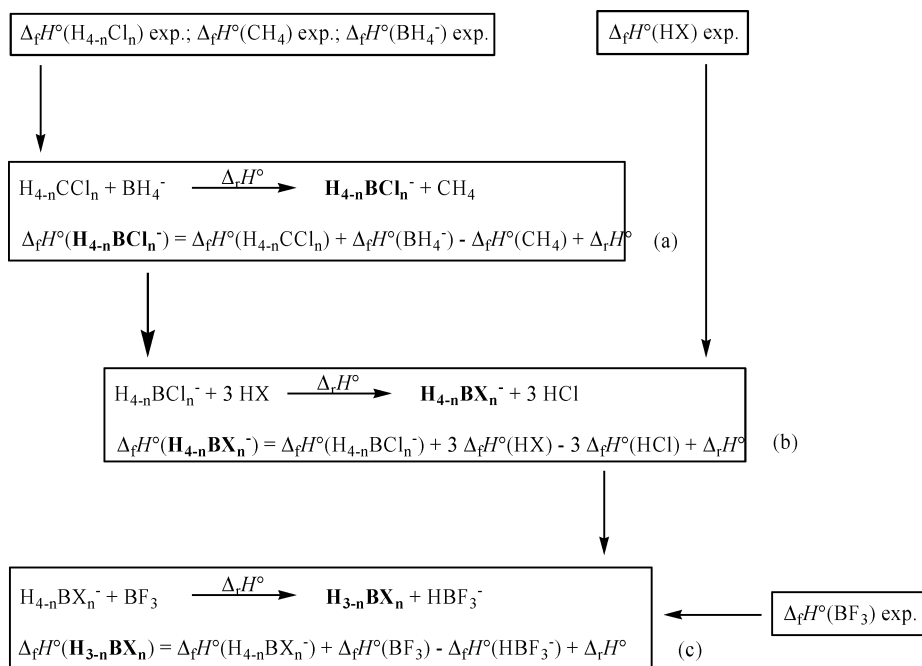
Enthalpies of Formation and Mean Bond Enthalpies

J. Phys. Chem. A, Vol. 111, No. 50, 2007 **13211**

SCHEME 2: Strategy to Obtain $\Delta_f H°$ of Haloboranes and Haloborate Anions

$\Delta_f H°(H_{4-n}Cl_n)$ exp.; $\Delta_f H°(CH_4)$ exp.; $\Delta_f H°(BH_4^-)$ exp.

$\Delta_f H°(HX)$ exp.

$$H_{4-n}CCl_n + BH_4^- \xrightarrow{\Delta_r H°} H_{4-n}BCl_n^- + CH_4$$

$\Delta_f H°(\mathbf{H_{4-n}BCl_n^-}) = \Delta_f H°(H_{4-n}CCl_n) + \Delta_f H°(BH_4^-) - \Delta_f H°(CH_4) + \Delta_r H°$ (a)

$$H_{4-n}BCl_n^- + 3\,HX \xrightarrow{\Delta_r H°} H_{4-n}BX_n^- + 3\,HCl$$

$\Delta_f H°(\mathbf{H_{4-n}BX_n^-}) = \Delta_f H°(H_{4-n}BCl_n^-) + 3\,\Delta_f H°(HX) - 3\,\Delta_f H°(HCl) + \Delta_r H°$ (b)

$$H_{4-n}BX_n^- + BF_3 \xrightarrow{\Delta_r H°} H_{3-n}BX_n + HBF_3^-$$

$\Delta_f H°(BF_3)$ exp.

$\Delta_f H°(\mathbf{H_{3-n}BX_n}) = \Delta_f H°(H_{4-n}BX_n^-) + \Delta_f H°(BF_3) - \Delta_f H°(HBF_3^-) + \Delta_r H°$ (c)

TABLE 1: Basis-Set Dependence of the Homolytic Dissociation Enthalpies $\Delta H°$ of the F_2 Molecule (according to Scheme 1a) at the ccsd(t) Level and Comparison with the G3 and the Experimental Values where All Values Are Given in Kilojoules per Mole

reaction	ccsd(t)/ aug-cc-pVDZ	ccsd(t)/ aug-cc-pVTZ	ccsd(t)/ aug-cc-pVQZ	ccsd(t)/ CBS[10]	G3	exptl value
$F_2 \rightarrow 2\,F^\bullet$	111	143	151	152	155	159[11]

TABLE 2: Overview of Various Experimental Values for $\Delta_f H°$ of the CF_3^+ Cation where AE = Appearance Energy, IE = Ionization Energy, PI = Photoionization, END = Determination of the Endothermicity of the Reaction, PIPECO = Photoion–Photoelectron Coincidence Spectroscopy

$\Delta_f H°(CF_3^+)$ [kJ mol^{-1}]	method	source
365	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_4)$	11
449	from $\Delta_f H°(HCF_3)$ and $\Delta_f H°(H)$	11
359	from $\Delta_f H°(CF_3)$ and $IE(CF_3)$	11,12
408	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3Cl$ and $CF_3Br)$	13
< 362	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3Cl)$	14
414	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3Cl)$	15
361	PI/END, from $AE(CF_3^+)$ and $\Delta_f H°(CF_4)$	12
391	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3Cl)$	16
359	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3Br)$	17
408	PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3I)$	18
399	PIPECO, PI, from $AE(CF_3^+)$ and $\Delta_f H°(CF_3I)$	19

of the particles were hitherto not accessed by quantum chemistry or at least not with the accuracy included herein, and the entries in Table 3 should aid for further studies.

2.3. Anchor Points. $\Delta_f H°$ of $H_{4-n}CX_n$ and $H_{3-n}CX_n^+$ (n = 1–3). For the calculations of $\Delta_f H°$ of $H_{4-n}CX_{4-n}$ and $H_{3-n}CX_n^+$ (n = 1–3), HCCl$_3$, H$_2$CCl$_2$, H$_3$CCl, and HX (X = F–I)[11] (Table 4) were taken as fix points, as their $\Delta_f H°$ values are measured very well on experimental grounds. $\Delta_f H°$ of the CF_3^+ cation has been established at the G3 level by the equation in Scheme 1a.

$\Delta_f H°$ of $H_{4-n}BX_n^-$ and $H_{3-n}BX_n$ (n = 1–3). The $\Delta_f H°$ values of $H_{4-n}BX_n^-$ (n = 1–3) could, in principle, be obtained analogously to those of the isoelectronic carbon compounds,

but as there are no reliable experimental data available, which could serve as fix points, the values for $H_{4-n}BCl_n^-$ have to be established first by the set of isodesmic reactions shown in Scheme 2a, using the experimental $\Delta_f H°$ values of CH$_4$ and $H_{4-n}CCl_{4-n}$ (n = 1–3) (BH$_4^-$: the ccsd(t)/aug-cc-pVTZ value of Dixon and Gutowski has been used[36]) together with the $\Delta_r H°$ at the G3 level. The values obtained by these reactions are listed in Table 5, together with that of BF$_3$, which is used as reference point for the calculations of the neutral boron species.

With these values, $\Delta_f H°$ of $H_{4-n}BX_n^-$ and $H_{3-n}B_n$ can then be calculated in an analogous way to those of the carbon compounds, like described in Scheme 2b,c.

$\Delta_f H°$ of Small Particles. The enthalpies of formation $\Delta_f H°$ of small, neutral carbon-containing species like C, CH, CH$_2$, and CH$_3$ as well as those of the halogens have been determined experimentally in very high accuracy,[11] and therefore, these values can be used as anchor points for this study. Also, their adiabatic ionization energies are available,[37,38] which gives an access to the $\Delta_f H°$ of their cations C$^+$, CH$^+$, CH$_2^+$, and CH$_3^+$. These values are listed in Table 6.

For the analogous boron compounds BH$^-$, BH$_2^-$, BH$_3^-$, B, BH, and BH$_2$, the experimental data are not very reliable, so that it seemed more accurate to calculate them using the following isodesmic equations at the G3 level and the experimental $\Delta_f H°$ values of the carbon-containing species and for BH$_4^-$, the value calculated by Dixon and Gutowski (-56 kJ mol^{-1}).[36] For BH$^-$, this step is shown in eq 5; for the other species, the reactions are given in Supporting Information.

$$BH_4^- + CH \xrightarrow{\Delta_r H°} CH_4 + BH^-$$
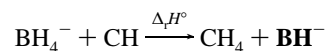
$$\Delta_f H°(\mathbf{BH^-}) = \Delta_f H°(BH_4^-) + \Delta_f H°(CH) - \Delta_f H°(CH_4) + \Delta_r H° \quad (5)$$

All values for $\Delta_f H°$ of the small particles obtained from these reactions are also collected in Table 6.

2.4. $\Delta_f H°$ of $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F–I). As already described above in Schemes 1 and 2, the $\Delta_f H°$ of $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F–I) can be

13212 *J. Phys. Chem. A, Vol. 111, No. 50, 2007*

Raabe et al.

TABLE 3: Calculated Structural Parameters (ccsd(t)/(SDB-)aug-cc-pVTZ) of $_nEX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F–I)[a]

particle	sym.	d(E–X) [pm] calcd	d(E–X) [pm] exptl	d(E–H) [pm] calcd	d(E–H) [pm] exptl	<HEH [°] calcd	<HEH [°] exptl	<HEX [°] calcd	<HEX [°] exptl	<XEX [°] calcd	<XEX [°] exptl
BF_3	D_{3h}	131.53	131.3[21]							120	120[21]
BCl_3	D_{3h}	174.67	175[3]							120	120[3]
BBr_3	D_{3h}	190.22	189.8[22]							120	120[22]
BI_3	D_{3h}	212.74	212.5[22]							120	120[22]
CF_3^+	D_{3h}	123.43	n.a.							120	n.a.
CCl_3^+	D_{3h}	165.47	162.1[3]							120	120[3]
CBr_3^+	D_{3h}	181.59	180.7[3]							120	120[3]
CI_3^+	D_{3h}	204.00	201.3[2] 200.6[2,4]							120	120[2,4]
HBF_2	C_{2v}	131.91	131.5[23]	118.59	119.5[23]			123.8	124.0[23]	118.1	118.0[23]
$HBCl_2$	C_{2v}	174.43	173.5[24]	118.27	118.4[24]			119.7	119.2[24]	120.7	120.4[24]
$HBBr_2$	C_{2v}	189.61	n.a.	118.24	n.a.			119.3	n.a.	121.4	n.a.
HBI_2	C_{2v}	211.50	n.a.	118.30	n.a.			118.6	n.a.	122.8	n.a.
HCF_2^+	C_{2v}	123.35	n.a.	109.41	n.a.			120.9	n.a.	118.1	n.a.
$HCCl_2^+$	C_{2v}	163.10	n.a.	108.89	n.a.			118.2	n.a.	123.6	n.a.
$HCBr_2^+$	C_{2v}	178.54	n.a.	108.79	n.a.			117.5	n.a.	125.0	n.a.
HCI_2^+	C_{2v}	199.98	n.a.	108.73	n.a.			116.4	n.a.	127.3	n.a.
H_2BF	C_{2v}	132.46	131.5[25]	119.34	119.7[25]	124.3	124.6[25]	117.8	117.7[25]		
H_2BCl	C_{2v}	174.65	173.5[26]	118.65	119.2[26]	123.9	124.2[26]	118.1	117.9[26]		
H_2BBr	C_{2v}	189.69	n.a.	118.57	n.a.	124.2	n.a.	117.9	n.a.		
H_2BI	C_{2v}	211.39	n.a.	118.52	n.a.	124.3	n.a.	117.8	n.a.		
H_2CF^+	C_{2v}	123.40	n.a.	109.35	n.a.	126.0	n.a.	117.0	n.a.		
H_2CCl^+	C_{2v}	160.07	n.a.	108.85	n.a.	122.0	n.a.	119.0	n.a.		
H_2CBr^+	C_{2v}	174.89	n.a.	108.71	n.a.	121.8	n.a.	119.1	n.a.		
H_2CI^+	C_{2v}	195.58	n.a.	108.58	n.a.	121.0	n.a.	119.5	n.a.		
HBF_3^-	C_{3v}	142.17	n.a.	123.39	n.a.			110.5	n.a.	108.5	n.a.
$HBCl_3^-$	C_{3v}	188.70	n.a.	119.60	n.a.			109.5	n.a.	109.4	n.a.
$HBBr_3^-$	C_{3v}	204.38	n.a.	119.08	n.a.			109.0	n.a.	109.9	n.a.
HBI_3^-	C_{3v}	226.44	n.a.	118.77	n.a.			108.0	n.a.	110.9	n.a.
HCF_3	C_{3v}	133.63	132.8[27]	108.82	109.1[27]			110.5	n.a.	108.4	108.6[27]
$HCCl_3$	C_{3v}	177.19	175.8[28]	108.22	110.0[28]			108.0	113.3[28]	110.9	n.a.
$HCBr_3$	C_{3v}	192.96	192.4[29]	108.17	111.0[29]			107.3	107.2[29]	111.6	111.7[29]
HCI_3	C_{3v}	214.78	211[30]	108.31	109[30]			106.2	103.7[30]	112.6	114.6[30]
$H_2BF_2^-$	C_{2v}	144.11	n.a.	124.24	n.a.	111.9	n.a.	109.2	n.a.	108.0	n.a.
$H_2BCl_2^-$	C_{2v}	192.11	n.a.	120.52	n.a.	115.5	n.a.	108.0	n.a.	109.3	n.a.
$H_2BBr_2^-$	C_{2v}	208.15	n.a.	119.96	n.a.	117.2	n.a.	107.4	n.a.	109.7	n.a.
$H_2BI_2^-$	C_{2v}	230.06	n.a.	119.54	n.a.	118.2	n.a.	107.0	n.a.	111.0	n.a.
H_2CF_2	C_{2v}	135.96	135.1[27]	109.00	108.4[27]	113.5	112.8[27]	108.7	n.a.	108.2	108.5[27]
H_2CCl_2	C_{2v}	177.72	177.2[31]	108.42	106.8[31]	112.0	118.8[31]	108.2	n.a.	112.3	112.0[31]
H_2CBr_2	C_{2v}	193.06	193.0[32]	108.32	107.9[32]	112.3	113.6[32]	107.8	n.a.	113.2	113.0[32]
H_2CI_2	C_{2v}	214.05	213.4[33]	108.35	107.8[34]	111.8	113.3[34]	107.6	n.a.	114.9	114.0[33]
H_3BF^-	C_{3v}	146.62	n.a.	124.32	n.a.	109.2	n.a.	109.7	n.a.		
H_3BCl^-	C_{3v}	198.11	n.a.	121.94	n.a.	112.3	n.a.	106.4	n.a.		
H_3BBr^-	C_{3v}	216.06	n.a.	121.45	n.a.	113.6	n.a.	105.0	n.a.		
H_3BI^-	C_{3v}	239.74	n.a.	121.00	n.a.	114.7	n.a.	103.5	n.a.		
H_3CF	C_{3v}	138.88	138.2[27]	109.06	109.0[27]	110.2	110.5[27]	108.7	n.a.		
H_3CCl	C_{3v}	179.20	177.8[35]	108.65	108.6[35]	110.7	110.4[35]	108.2	n.a.		
H_3CBr	C_{3v}	194.41	193.3[35]	108.57	108.6[35]	111.2	111.1[35]	107.7	n.a.		
H_3CI	C_{3v}	214.85	213.3[35]	108.56	108.5[35]	111.4	111.2[35]	107.4	n.a.		

[a] n.a. = value not available in the literature.

TABLE 4: $\Delta_f H°$ of $H_{4-n}CCl_n$ (n = 1–3), HX (X = F–I), and CF_3^+ where All Values Are Given in Kilojoules per Mole

particle	$\Delta_f H°$	method
$HCCl_3$	−103	exp.[11]
H_2CCl_2	−96	exp.[11]
H_3CCl	−84	exp.[11]
HF	−273	exp.[11]
HCl	−92	exp.[11]
HBr	−36	exp.[11]
HI	26	exp.[11]
CF_3^+	410	calc. G3

TABLE 5: $\Delta_f H°$ of $H_{4-n}BCl_n^-$ (n = 1–3), BH_4^-, and BF_3 According to Scheme 2a where All Values Are Given in Kilojoules per Mole

particle	$\Delta_f H°$	reaction/method
H_3BCl^-	−268	$H_3CCl + BH_4^- \rightarrow H_3BCl^- + CH_4$/G3
$H_2BCl_2^-$	−469	$H_2CCl_2 + BH_4^- \rightarrow H_2BCl_2^- + CH_4$/G3
$HBCl_3^-$	−655	$HCCl_3 + BH_4^- \rightarrow HBCl_3^- + CH_4$/G3
BF_3	−1136	exp.[11]

established through a set of isodesmic reactions. In the following tables (Table 7 through Table 10), the reaction enthalpies obtained by different methods are collected. As it can be seen, for the most part of the reactions the MP2/TZVPP values are in the same order of magnitude (max. deviation: 27 kJ mol⁻¹) than those from ccsd(t) or G3 calculations. However, the latter

two methods are more accurate and will therefore be used in the discussion. G3 will be used as a reference for compounds containing F and Cl. For Br and I containing species, the G3 method cannot be used, and therefore, ccsd(t)/(SDB-)aug-cc-pVTZ values are used as reference values.

3. Discussion

Enthalpies of Formation $\Delta_f H°$. With the reaction enthalpies collected in Tables 7–10 and the auxiliary data in Tables 4–6,

Enthalpies of Formation and Mean Bond Enthalpies

J. Phys. Chem. A, Vol. 111, No. 50, 2007 **13213**

TABLE 6: Experimental $\Delta_f H°$ of CH_n, CH_n^+ ($n = 0-3$), X, and X^+ (X = F$-$I) and Calculated Values for $\Delta_f H°$ of BH_n^- ($n = 1-4$), BH_n ($n = 0-3$; G3 Method); All Values Are Given in Kilojoules per Mole; Values Used in This Study Are Marked in Bold; Direct = Value Directly Taken from the Reference

	$\Delta_f H°$			$\Delta_f H°$	
particle	G3	exptl	particle	G3	exptl
C		**717**[11]	C^+		**1803**[11,38 a]
CH (dublet)		**549**[11]	CH^+ (singlet)		**1621**[11,37 b]
CH_2 (triplet)		**368**[11]	CH_2^+		**1372**[11,38 c]
CH_3		**146**[11]	CH_3^+		**1095**[11,39 d]
BH_4^-		-77[40 g]	B	**579**[h]	560
BH (singlet)	**446**	443[11]	BH^- (dublet)	**419**	414[11,41 e]
BH_2	**310**	201[11]	BH_2^- (singlet)	**262**	
BH_3		107[11]	BH_3^-	**86**	84[42 f]
F		**79**[11]	Br		**112**[11]
Cl		**121**[11]	I		**107**[11]

^{a} $\Delta_f H°(C) + IE(C)$. ^{b} $\Delta_f H°(CH) + IE(CH)$. ^{c} $\Delta_f H°(CH_2) + IE(CH_2)$. ^{d} $\Delta_f H°(CH_3) + IE(CH_3)$. ^{e} $\Delta_f H°(BH) + EA(BH)$. ^{f} $\Delta_f H°(BH_3) + EA(BH_3)$. ^{g} -56 kJ mol^{-1} from ccsd(t)/aug-cc-pVTZ from ref 36 has been used. ^{h} Calculated via the isodesmic reaction $BH_3 + C^+ \rightarrow CH_3^+ + B$ at the G3 level using the expperimental $\Delta_f H°$ values of C^+, CH_3^+, and BH_3.

TABLE 7: Calculated Enthalpies ($\Delta_r H°$ in kJ mol^{-1}) According to Scheme 1b where the Best Values Are Marked in Bold

	MP2/ TZVPP	ccsd(t)/ (SDB-)aug- cc-pVTZ	G3
$H_3CCl + HX \rightarrow H_3CX + HCl$			
F	30	20	**26**
Cl	0	0	**0**
Br	-11	**-11**	
I	-26	**-23**	
$H_2CCl_2 + 2HX \rightarrow H_2CX_2 + 2HCl$			
F	9	-8	**4**
Cl	0	0	**0**
Br	-17	**-18**	
I	-46	**-36**	
$HCCl_3 + 3HX \rightarrow HCX_3 + 3HCl$			
F	-47	-66	**-51**
Cl	0	0	**0**
Br	-22	**-23**	
I	-65	**-46**	

TABLE 8: Calculated Enthalpies ($\Delta_r H°$ in kJ mol^{-1}) According to Scheme 1c where the Best Values Are Marked in Bold

	MP2/ TZVPP	ccsd(t)/ (SDB-)aug- cc-pVTZ	G3
$H_3CX + CF_3^+ \rightarrow HCF_3 + H_2CX^+$			
F	-21	-34	**-28**
Cl	-52	-34	**-70**
Br	-58	**-83**	
I	-83	**-108**	
$H_2CX_2 + CF_3^+ \rightarrow HCF_3 + HCX_2^+$			
F	-55	-59	**-56**
Cl	-112	-124	**-127**
Br	-123	**-140**	
I	-159	**-173**	
$HCX_3 + CF_3^+ \rightarrow HCF_3 + CX_3^+$			
F	0	0	**0**
Cl	-144	-150	**-157**
Br	-165	**-175**	
I	-211	**-217**	

TABLE 9: Calculated Enthalpies ($\Delta_r H°$ in kJ mol^{-1}) According to Scheme 2b where the Best Values Are Marked in Bold

	MP2/ TZVPP	ccsd(t)/ (SDB-)aug- cc-pVTZ	G3
$H_3BCl^- + HX \rightarrow H_3BX^- + HCl$			
F	23	20	**24**
Cl	0	0	**0**
Br	-17	**-13**	
I	-36	**-29**	
$H_2BCl_2^- + 2HX \rightarrow H_2BX_2^- + 2HCl$			
F	-9	-21	**-10**
Cl	0	0	**0**
Br	-17	**-13**	
I	-36	**-23**	
$HBCl_3^- + 3HX \rightarrow HBX_3^- + 3HCl$			
F	-83	-102	**-85**
Cl	0	0	**0**
Br	-8	**-3**	
I	-21	**2**	

TABLE 10: Calculated Enthalpies ($\Delta_r H°$ in kJ mol^{-1}) According to Scheme 2c where the Best Values Are Marked in Bold

	MP2/ TZVPP	ccsd(t)/ (SDB-)aug- cc-pVTZ	G3
$H_3BX^- + BF_3 \rightarrow HBF_3^- + H_2BX$			
F	-28	-31	**-32**
Cl	43	42	**40**
Br	71	**61**	
I	100	**91**	
$H_2BX_2^- + BF_3 \rightarrow HBF_3^- + HBX_2$			
F	-42	-43	**-43**
Cl	69	71	**69**
Br	109	**100**	
I	144	**137**	
$HBX_3^- + BF_3 \rightarrow HBF_3^- + BX_3$			
F	0	0	**0**
Cl	98	102	**100**
Br	137	**131**	
I	168	**164**	

Only the values obtained with the most accurate method, that is, G3 for F and Cl and ccsd(t)/(SDB-)aug-cc-pVTZ for Br and I, are collected here.
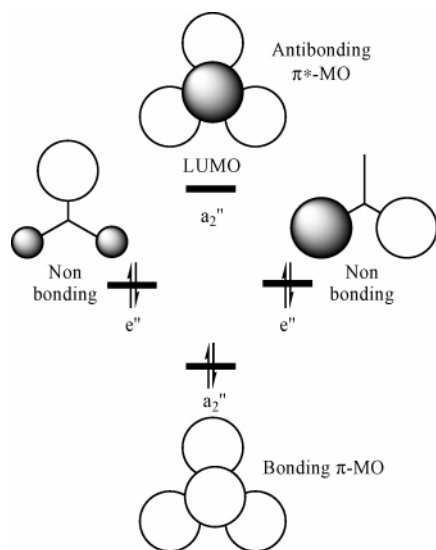
In 2005, Marshall et al. published a high-level computational study on the $\Delta_f H°$ of bromine and iodine-containing methanes,[9] based on isodesmic reactions using QCISD(T)/6-311+G(3df,-2p) energy values. The results of this study are also included in Table 11. Although different anchor points were chosen, the $\Delta_f H°$ obtained by Marshall et al. are in very good agreement with the values obtained from our calculations (max. difference: 10 kJ mol^{-1}, which is within the error bars given in ref 9), confirming the reliability of our data. Similarly, we judge our calculations to have a maximum error bar of about ± 10 kJ mol^{-1}.

Upon comparing the calculated data with (less accurate) available experimental values for some systems, like HCX_3 (X = Br, I), H_2CBr_2, CF_3^+, and BI_3, the experimentally found $\Delta_f H°$ differ considerably from the computed ones. In those cases, where several experimental values were found in the literature, they also scatter considerably (up to 90 kJ mol^{-1} for CF_3^+). For H_3CF and CI_3^+, the experimental values are in the same order of magnitude as the computed ones, but the difference is still too large to use them as a reliable reference. A very good agreement is also found for the HCF_3 molecule that we used as an anchor point: its experimental $\Delta_f H°$ value is -697 kJ mol^{-1} (this value has been used to establish the $\Delta_f H°$ of the CF_3^+

the enthalpies of formation $\Delta_f H°$ of all $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F$-$I) were established according to Schemes 1 and 2; the "best values" are listed in Table 11.

TABLE 11: $\Delta_f H°$ of All $H_{4-n}EX_n^{0/-}$ and $H_{3-n}EX_n^{+/0}$ (E = C, B; X = F–I); All Values Are Given in Kilojoules per Mole; Methods: G3 for F and Cl, ccsd(t)/(SDB-)aug-cc-pVTZ for Br and I; Anchor = Experimental Data Has Been Used as an Anchor Point for the Calculations in This Study

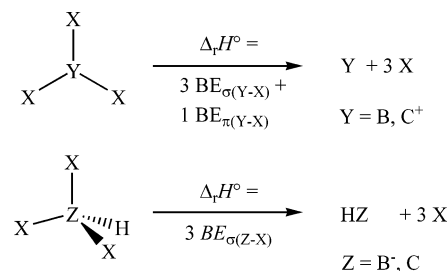|	X = F		X = Cl		X = Br		X = I	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
H_3CX	−258	−234[11]	anchor	−84[11]	−39	−38[43]; −36[44]; −38[45]; −38[46]; −36[47]; −34[48]	12	14[49]; 14[44]; 14[46]; 14[50]
H_2CX_2	−452	−451[11]	anchor	−96[11]	−2 (4[9])[a]	−36[43]; 4[51]; 10[44]; 3[45]; −15[46]; −11[47]; 6[52]	106 (108[9])[a]	118[46]; 108[45]; 120[50]; 122[53]
HCX_3	−695	−697[11]	anchor	−103[11]	42 (52[9])[a]	55[52]; 51[51]; 60[44]; 17[46]; 24[47]	205 (209[9])[a]	251[50,54]; 211[46]
H_3BX^-	−425		−268		−227		−181	
$H_2BX_2^-$	−839		−469		−371		−257	
HBX_3^-	−1282		−655		−492		−301	
H_2CX^+	826	838[11,55]; 827[11,55]	951	955[11,56]; 951[11,55]	997	988[11,57]; 1037[43,58]	1023	1029[46,59]; 1029[49,59]
HCX_2^+	596	559[11]	882	884[11]	975	976[11,51]	1049	1087[57]
CX_3^+	410	365[11]; 449[11]; 359[11,12]; 408[13]; < 362[14]; 414[15]; 361[12]; 391[16]; 359[17]; 408[18]; 399[19]	844	862[11]; 871[11,60]; 859[61]	981	1031[11,62]; 995[11,63]; 992−999[6]	1103	∼1047[b]
H_2BX	−311	-	−83		−10		66	
HBX_2	−737	−734[11]	−255	−248[11]	−113	−105[11]	39	
BX_3	anchor	−1136[11]	−410	−403[11]	−203	−204[11]	21	71[11]

[a] At the QCISD(T)/6-311+G(3df,2p) level, from ref 9. [b] J. M. L. Abboud, personal communication. The value of 531 kJ mol^{-1} given in ref 6 is wrong.

Figure 2. Top view of the π MOs of $EX_3^{0/+}$.

Figure 3. σ and π contributions to the E–X bonds in $EX_3^{0/+}$ and $HEX_3^{-/0}$.

TABLE 12: mBEs of $H_{4-n}CX_n$ and $H_{4-n}BX_n^-$ ($n = 1-3$) in Kilojoules per Mole

X =	H_3CX	H_2CX_2	HCX_3	H_3BX^-	$H_2BX_2^-$	HBX_3^-
F	483	490	509	611	641	653
Cl	351	353	354	496	497	486
Br	297	297	296	444	439	422
I	240	238	236	392	376	353

TABLE 13: mBEs of $H_{3-n}CX_n^+$ and $H_{3-n}BX_n$ ($n = 1-3$) in Kilojoules per Mole

X =	H_2CX^+	HCX_2^+	CX_3^+	H_2BX	HBX_2	BX_3
F	627	589	542	700	671	651
Cl	536	488	439	514	471	444
Br	479	430	382	424	389	371
I	448	388	336	342	307	290

cation), and our calculated $\Delta_f H°$ value is −695 kJ mol^{-1}. This cross-check underlines the consistency of our method. For the $H_{4-n}BX_n^-$, H_2BX (X = Cl–I), and HBI_2, there are no experimental data available to the best of our knowledge (SciFinder and NIST database search). Except for the carbenium ions, the iodomethanes, and the iodoboranes, all particles have a negative enthalpy of formation.

In each of the series, the $\Delta_f H°$ values increase from fluorine to iodine, and except for the iodine-containing carbenium ions and the bromo- and iodomethanes, the $\Delta_f H°$ becomes lower with the more halogen atoms that are present in the particle. The boron containing species always have a lower $\Delta_f H°$ than the isoelectronic carbenium ions and methanes, and the $H_{4-n}EX_n^{-/0}$ are lower in energy than the parent $H_{3-n}EX_n^{+/0}$. This reflects the greater average B–X bond strengths (see mBEs below).

Mean E-X bond enthalpies (E = B, C). To obtain the mBEs of the species, the values of the reaction enthalpies from eq 1 to eq 4 have to be divided by the number of E–X bonds that are cleaved. The results, using the $\Delta_f H°$ values listed in Table 6 and Table 11, are collected in Tables 12 and 13.

As it can bee seen, in all species, the mBE decreases from fluorine to iodine, which is consistent with the electronegativities of the halogens. For all halomethyl cations and haloboranes, the mBEs are lowered, if a series contains more halogen atoms; for the $H_{4-n}EX_n^{0/+}$, they remain nearly unchanged upon replacing H by X. The only two exceptions are the fluoromethanes and fluoroborates, where the mBE is increased if more fluorine atoms are present. Again, this is due to the high electronegativity of fluorine, which causes electrostatic interactions and therefore strengthens the E–F bond.

Especially for the haloborates, the values of the mBEs are very high. The highest mBE of the haloborates of 653 kJ mol^{-1} is found for HBF_3^-. However, by definition, eqs 1−4 are the only way to determine mBEs for these compounds. The different bond strengths in the isoelectronic boron and carbon containing

Enthalpies of Formation and Mean Bond Enthalpies

J. Phys. Chem. A, Vol. 111, No. 50, 2007 **13215**

TABLE 14: $\Delta_r H°$ Values (in kJ mol^{-1}) for the Reaction Described in Eqs 6 and 7

	$\Delta_r H°$		$\Delta_r H°$
$CF_3^+ + B \rightarrow BF_3 + C^+$	-327	$HCF_3 + B^- \rightarrow HBF_3^- + C$	-443
$CCl_3^+ + B \rightarrow BCl_3 + C^+$	-16	$HCCl_3 + B^- \rightarrow HBCl_3^- + C$	-408
$CBr_3^+ + B \rightarrow BBr_3 + C^+$	35	$HCBr_3 + B^- \rightarrow HBBr_3^- + C$	-388
$CI_3^+ + B \rightarrow BI_3 + C^+$	138	$HCI_3 + B^- \rightarrow HBI_3^- + C$	-360
$HCF_2^+ + B \rightarrow HBF_2 + C^+$	-114	$H_2CF_2 + B^- \rightarrow H_2BF_2^- + C$	-243
$HCCl_2^+ + B \rightarrow HBCl_2 + C^+$	82	$H_2CCl_2 + B^- \rightarrow H_2BCl_2^- + C$	-229
$HCBr_2^+ + B \rightarrow HBBr_2 + C^+$	132	$H_2CBr_2 + B^- \rightarrow H_2BBr_2^- + C$	-224
$HCI_2^+ + B \rightarrow HBI_2 + C^+$	211	$H_2CI_2 + B^- \rightarrow H_2BI_2^- + C$	-259
$H_2CF^+ + B \rightarrow H_2BF + C^+$	90	$H_3CF + B^- \rightarrow H_3BF^- + C$	-23
$H_2CCl^+ + B \rightarrow H_2BCl + C^+$	185	$H_3CCl + B^- \rightarrow H_3BCl^- + C$	-41
$H_2CBr^+ + B \rightarrow H_2BBr + C^+$	218	$H_3CBr + B^- \rightarrow H_3BBr^- + C$	-43
$H_2CI^+ + B \rightarrow H_2BI + C^+$	269	$H_3CI + B^- \rightarrow H_3BI^- + C$	-47

species and possible reasons for these differences will be discussed in the following section.

Relative E–X Bond Strengths in the Isoelectronic $H_{3-n}CX_n^+/H_{3-n}BX_n$ and $H_{4-n}CX_n/H_{4-n}BX_n^-$ ($n = 1-3$) Pairs. For the trihaloboranes and trihalocarbenium ions, it is clear that the following π molecular orbitals (MOs) are formed and that the lowest unoccupied molecular orbital (LUMO) of all BX_3 as well as CX_3^+ particles corresponds to the π^* MO of a_2'' symmetry, compared with the top view of the MOs of π symmetry in BX_3 and CX_3^+ in Figure 2.

The bonding π MO (a_2'') is occupied for all of those particles. Similar MO considerations hold for the partly H-substituted particles $H_{3-n}EX_n^{0/+}$. However, no quantification of the amount of stabilization by π bonding is possible only on the basis of the presence of an occupied π MO. Thus, alternative quantitative approaches have to be adopted, like, for example, the comparison of the mBEs in the isoelectronic boron and carbon containing species.

In Figure 3, the different contributions, that is, σ and π, to the E–X bonds in $EX_3^{0/+}$ and $HEX_3^{-/0}$ are sketched. For the other particles, analogous schemes can be drawn.

On the basis of experimental observations as well as on quantum chemical calculations, it is postulated in the literature that, in halocarbenium ions, the positive charge is delocalized over the entire cation and, especially for the heavier halogens, leads to a formation of strong π bonds.[2,4,8,64] However, until now, no quantitative information on the strengths of these π bonds is available. In this study, a comparison of the bond energies in $H_{3-n}CX_n^+$ with those of the isoelectronic $H_{3-n}BX_n$ is made on the basis of their $\Delta_f H°$. To find out if the E–X bond is stronger in the $H_{3-n}CX_n^+$ cations or in $H_{3-n}BX_n$, the C–B exchange reaction enthalpy of the following reaction has been calculated using the $\Delta_f H°$ values:

$$H_nCX_{3-n}^+ + B \xrightarrow{\Delta_r H°} H_nBX_{3-n} + C^+ \qquad (6)$$

In these reactions, all C–X bonds are cleaved, while the same number of B–X bonds is created. The reaction enthalpy $\Delta_r H°$ (Table 14) directly corresponds to the difference of the E–X bond energies. As a cross reference, the same has been done for the pairs $H_{4-n}CX_n$, $H_{4-n}BX_n^-$ ($n = 1-3$), where no π bonding is expected (eq 7).

$$H_nCX_{4-n} + B^- \xrightarrow{\Delta_r H°} H_nBX_{4-n}^- + C \qquad (7)$$

In the case of the halocarbenium ions/haloboranes, the reaction enthalpies $\Delta_r H°$ strongly increase from F to I, while for the halomethane/haloborate pairs, they remain nearly unchanged upon halogen variation. One notes the strongly increasing stability of the heavier halocarbenium ions. To our understanding, this can only be explained with stronger π

bonding in the heavier halocarbenium ions with reference to the haloboranes. Thus, B–F bonds in all $H_{3-n}EF_n^{+/0}$ particles (E = C, B) that may exhibit π bonding are always stronger than C–F bonds, but C–X bonds of $H_{3-n}EX_n^{+/0}$ (E = C, B; X = Cl–I) are always stronger than B–X bonds with the only exception of CCl_3^+ and BCl_3 which have almost identical mBEs. By contrast, the differences between the E–X bond strengths in the analogous saturated $H_{4-n}EX_n^{-/0}$ compounds with only σ bonding are less affected by exchanging C for B$^-$ and always in favor of B–X bonds (X = F–I).

4. Conclusion

In this study, reliable $\Delta_f H°$ values for halomethanes, halomethyl cations, and the isoelectronic boron compounds have been established on the basis of a combination of exactly determined experimental data together with highly correlated quantum chemical calculations.

When going from fluorine to iodine, the $\Delta_f H°$ values increase in each series of species, and except for the iodine-containing carbenium ions and the bromo- and iodomethanes, the $\Delta_f H°$ is lower the more halogen atoms are present in the particle. The boron containing species always have a lower $\Delta_f H°$ than the isoelectronic carbenium ions and methanes, and the $H_{4-n}EX_n^{-/0}$ are lower in energy than the parent $H_{3-n}EX_n^{+/0}$. The trends of the mBE values can be explained by the electronegativity of the halogens. Specifically, the heavier halocarbenium ions are very stable if compared with the isoelectronic haloboranes, indicating strong π bonding.

5. Computational Details

Calculations including geometry optimizations have been performed with the program package Turbomole 5.8[65] (MP2/TZVPP[66]) and with Gaussian 03[67] (ccsd(t)). ZPEs were obtained using the module AOFORCE[68] in Turbomole (at the (RI)BP86/SV(P) level[69]). If not mentioned otherwise in the text, for ccsd-(t) calculations, the aug-cc-pVTZ basis set[70] was used (SDB-aug-cc-PVTZ[71] with relativistic ECPs for Br (ECP28MWB) and I (ECP46MWB)[72]), while for the other particles, the calculations were done at the G3 level.[73] Open shell molecules were calculated using unrestricted wavefunctions. All basis sets used in this study have been obtained from the EMSL Gaussian Basis Set order form.[74]

Supporting Information Available: Reactions leading to the mBEs as well as the geometries, energies (at different levels of theory), and ZPEs of all calculated particles are deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shriver, D. F.; Swanson, B. *Inorg. Chem.* **1971**, *10*, 1354; Brown, H. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1956**, *78*, 2173; Sreekanth, C. S.; Mok, C. Y.; Huang, H. H. *J. Elect. Spectrosc. Relat. Phenom.* **1992**, *58*, 129; Cotton, F. A.; Wilkinson, G. *Advances Inorganic Chemistry*; John Wiley and Sons: New York, 1980; Liebman, J. F. *Struct. Chem.* **1990**, *1*, 395; Rothe, E. W.; Mathur, B. P.; Reck, G. P. *Inorg. Chem.* **1980**, *19*, 829; Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801; Buslaev, Y. A.; Kravchenko, E. A.; Kolditz, L. *Coord. Chem. Rev.* **1987**, *82*, 3; Branchadell, V.; Oliva, A. *Theochem* **1991**, *82*, 75.

(2) Krossing, I.; Bihlmeier, A.; Raabe, I.; Trapp, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1531.

(3) Mercier, H. P. A.; Moran, M. D.; Schrobilgen, G. J.; Suontamo, R. J. *J. Fluorine Chem.* **2004**, *125*, 1563.

(4) Raabe, I.; Müller, S.; Trapp, N.; Kaupp, M.; Krossing, I. *Dalton Trans.* **2007**, in press.

(5) Mercier, H. P. A.; Moran, M. D.; Schrobilgen, G. J.; Steinberg, C.; Suontamo, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 5533; Christe, K. O.; Hoge, B.; Boatz, J. A.; Prakash, G. K. S.; Olah, G. A.; Sheehy, J. A. *Inorg. Chem.* **1999**, *38*, 3132.

(6) Abboud, J. L. M.; Castano, O.; Herreros, M.; Elguero, J.; Jagerovic, N.; Notario, R.; Sak, K. *Int. J. Mass Spectrom. Ion Processes* **1998**, *175*, 35.

(7) Olah, G. A. *Friedel-Crafts Chemistry (Interscience Monographs on Organic Chemistry)*; Wiley & Sons: New York, 1973; Olah, G. A. *Angew. Chem.* **1973**, *85*, 183; Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580; Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446.

(8) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648.

(9) Marshall, P.; Srinivas, G. N.; Schwartz, M. *J. Phys. Chem. A* **2005**, *109*, 6371.

(10) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154; Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669; Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136.

(11) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *27*.

(12) Fischer, E. R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 1.

(13) Asher, R. L.; Ruscic, B. *J. Chem. Phys.* **1997**, *106*, 210.

(14) Noutary, C. J. *J. Res. Natl. Bur. Stand. (U.S.)* **1968**, *72A*, 479.

(15) Powis, I. *Mol. Phys.* **1980**, *39*, 311.

(16) Ajello, J. M.; Huntress, W. T., Jr.; Rayermann, P. *J. Chem. Phys.* **1976**, *64*, 4746.

(17) Clay, T. J.; Walters, E. A.; Grover, J. R.; Willcox, M. V. *J. Chem. Phys.* **1994**, *101*, 2069.

(18) Berman, D. W.; Beauchamp, J. L. *Int. J. Mass Spectrom.* **1981**, *39*, 47.

(19) Bombach, R.; Dannacher, J.; Stadelmann, J.-P.; Vogt, J.; Thorne, L. R.; Beauchamp, J. L. *Chem. Phys.* **1982**, *66*, 403.

(20) Dixon, D. A.; Feller, D.; Sandrone, G. *J. Phys. Chem. A* **1999**, *103*, 4744.

(21) Kuchizu, K.; Konaka, S. *J. Chem. Phys.* **1966**, *45*, 4342.

(22) Krossing, I.; Santiso, G., *Z. Anorg. Allg. Chem.* **2007**, in press.

(23) Robiette, A. G.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1980**, *80*, 403.

(24) Sugie, M.; Takeo, H.; Matsumura, C. *Spectrochim. Acta A* **1994**, *50A*, 1379.

(25) Takeo, H.; Sugie, M.; Matsumura, C. *J. Mol. Spectrosc.* **1993**, *158*, 201.

(26) Kawashima, Y.; Takeo, H.; Sugie, M.; Matsumura, C.; Hirota, E. *J. Chem. Phys.* **1993**, *99*, 820.

(27) Kawashima, Y.; Cox, A. P. *J. Mol. Spectrosc.* **1978**, *72*, 423.

(28) Jen, M.; Lide, D. R., Jr. *J. Chem. Phys.* **1962**, *36*, 2525.

(29) Tamagawa, K.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2747.

(30) Iwata, Y.; Watanabe, T. *Annual Reports of the Research Reactor Institute*; Kyoto University **1974**, *7*, 87.

(31) Kawaguchi, T.; Tanaka, K.; Takeuchi, T.; Watanabe, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 62.

(32) Krishnaji, S. L. S.; Rajput, A. S. *Physics Lett. A* **1970**, *31*, 411.

(33) Kisiel, Z.; Pszczolkowski, L.; Caminati, W.; Favero, P. G. *J. Chem. Phys.* **1996**, *105*, 1778.

(34) Kisiel, Z.; Pszczolkowski, L.; Favero, L. B.; Caminati, W. *J. Mol. Spectrosc.* **1998**, *189*, 283.

(35) Duncan, J. L. *J. Mol. Struct.* **1970**, *6*, 447.

(36) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129.

(37) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, 4: Constants of Diatomic Molecules;* van Nostrand Reinhold Company: New York, 1979.

(38) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics 77th Edition*; CRC Press: Boca Raton, FL, 1996.

(39) Lias, S. G. *Ionization Energy Evaluation in: NIST Chemistry WebBook, NIST Standard Reference Database*; National Institute of Standards and Technology: Gaithersburg, MD, 2005; Vol. 69.

(40) Workman, D. B.; Squires, R. R. *Inorg. Chem.* **1988**, *27*, 1846.

(41) Reid, C. J. *Int. J. Mass Spectrom. Ion Processes* **1993**, *127*, 147.

(42) Wickham-Jones, C. T.; Moran, S.; Ellison, G. B. *J. Chem. Phys.* **1989**, *90*, 795.

(43) Fowell, P.; Lacher, J. R.; Park, J. D. *Trans. Faraday Soc.* **1965**, *61*, 1324.

(44) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individal Substances*, 4 ed.; Hemisphere: New York, 1992.

(45) Lago, A. F.; Kercher, J. P.; Bödi, A.; Sztáray, B.; Miller, B.; Wurzelman, D.; Baer, T. *J. Phys. Chem. A* **2005**, *109*, 1802.

(46) Kudchadker, S. A.; Kudchadker, A. P. *J. Phys. Chem. Ref. Data* **1976**, *5*, 529.

(47) Bickerton, J.; Da, Piedade, M. E. M.; Pilcher, G. *J. Chem. Thermodyn.* **1984**, *16*, 661.

(48) Ferguson, K. C.; Okafo, E. N.; Whittle, E. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 295.

(49) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(50) Carson, A. S.; Laye, P. G.; Pedley, J. B.; Welsby, A. M. *J. Chem. Thermodyn.* **1993**, *25*, 261.

(51) Paddison, S. J.; Tschuikow-Roux, E. *J. Phys. Chem. A* **1998**, *102*, 6191.

(52) Papina, T. S.; Kolesov, V. P.; Golovanova, Y. G. *Russ. J. Phys. Chem. (Engl. Transl.)* **1982**, *56*, 1666.

(53) Furuyama, S.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 4713.

(54) Nitta, I.; Seki, S. *J. Chem. Soc. Jpn.* **1943**, *64*, 475.

(55) Lossing, F. P. *Bull. Soc. Chim. Belg.* **1972**, *81*, 125.

(56) Harrison, A. G.; Shannon, T. W. *Can. J. Chem.* **1962**, *40*, 1730.

(57) Tsai, B. P.; Baer, T.; Werner, A. S.; Lin, S. F. *J. Phys. Chem.* **1975**, *79*, 570.

(58) Kaposi, O.; Riedel, M.; Vass-Balthazar, K.; Sanchez, G. R.; Lelik, L. *Acta Chim. Acad. Sci. Hung.* **1976**, *89*, 221.

(59) Holmes, J. L.; Lossing, F. P.; McFarlane, R. A. *Int. J. Mass Spectrom. Ion Phys.* **1988**, *86*, 209.

(60) Farmer, J. B.; Henderson, I. H. S.; Lossing, F. P.; Marsden, D. G. H. *J. Chem. Phys.* **1956**, *24*, 348.

(61) Hudgens, J. W.; Johnson, R. D.; Timonen, S.; Seetula, J. A.; Gutman, D. *J. Phys. Chem.* **1991**, *95*.

(62) Reed, R. I.; Snedden, W. *J. Chem. Soc., Faraday Trans.* **1958**, *54*, 301.

(63) Kime, Y. J.; Driscoll, D. C.; Dowben, P. A. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 403.

(64) Krossing, I.; Raabe, I. *J. Am. Chem. Soc.* **2004**, *126*, 7571.

(65) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(66) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331; Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143; Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571; Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(67) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision C02*; Gaussian, Inc.: Wallingford, CT, 2004.

Enthalpies of Formation and Mean Bond Enthalpies

J. Phys. Chem. A, Vol. 111, No. 50, 2007 **13217**

(68) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511.

(69) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098; Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B: Condens. Matter* **1996**, *54*, 16533; Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(70) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *110*, 7667; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358; Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796; Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007; Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099; Peterson, K.

A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.

(71) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408.

(72) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(73) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(74) EMSL Gaussian Basis Set order form, http://www.emsl.pnl.gov/forms/basisform.html.