

The π -Donor Ability of the Halogens in Cations and Neutral Molecules. A Theoretical Study of AX_3^+ , AH_2X^+ , YX_3 , and YH_2X (A = C, Si, Ge, Sn, Pb; Y = B, Al, Ga, In, Tl; X = F, Cl, Br, I)

Gernot Frenking,^{*,†} Stefan Fau,[†] Christina M. Marchand,[‡] and Hansjörg Grützmacher[‡]

Contribution from the *Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany, and the Laboratorium für Anorganische Chemie, Eidgenössische Technische Hochschule, Universitätsstrasse 6, CH-8092 Zürich, Switzerland*

Received January 31, 1997. Revised Manuscript Received May 5, 1997[⊗]

Abstract: Quantum mechanical ab initio calculations at the MP2/VDZ+P level of theory (for some molecules at MP2/VTZ+D+P) are reported for the cations AX_3^+ and AH_2X^+ (A = C, Si, Ge, Sn, Pb; X = F, Cl, Br, I) and the isoelectronic neutral Lewis acids YX_3 and YH_2X (Y = B, Al, Ga, In, Tl; X = F, Cl, Br, I). The π -donor ability of the halogens given by the $p(\pi)$ population at atom A increases for all cations with $F < Cl < Br < I$, which is the opposite to what has been reported in a recent study of Olah and co-workers (*J. Am. Chem. Soc.* **1996**, *118*, 3580). The same trend is found at the central atom Y of most neutral compounds, but the increase is less pronounced than for the cations. The calculated order of the energetic stabilization of the cations and neutral compounds by the halogens is less uniform, because the σ - and π -donation show different trends. The energies of isodesmic reactions and the $X_3A^+-OH_2$ complexation energies predict for the thermodynamic stabilization of the Y-conjugated cations the same trend as the π -donor ability, i.e. $F < Cl < Br < I$. The energy differences are much less for the isodesmic reactions of the singly substituted AH_2X^+ than for AX_3^+ . Fluorine has a higher stabilizing effect in CH_2F^+ than in CF_3^+ , because the σ -withdrawing strength of F leads to a large positive charge at the carbon atom of CF_3^+ . The complexation energies of the boron halides BX_3 show little differences for X_3B-OH_2 among the halogens, although the $p(\pi)$ population at boron increases clearly from fluorine to iodine. The hydride affinity, however, increases strongly from BF_3 to BI_3 and from BH_2F to BH_2I . The heavy-atom homologues of C^+ , i.e. Si^+ , Ge^+ , Sn^+ , Pb^+ , and those of B, i.e. Al, Ga, In, Tl, show the same trends for the halogens, but the $p(\pi)$ donation and the thermodynamic stabilization or destabilization is clearly less than for C^+ and B, respectively.

Introduction

A classical topic of inorganic and general chemistry is the strength of multiple bonds between main-group elements, which decreases when one goes from lighter to heavier elements. Quantum mechanical studies have shown that the decrease in the strength of multiple bonds between heavier atoms of the same group is *not* due to less overlap population of the π bond(s).¹ N_2 and P_2 have about the same $p(\pi)$ population.¹ The strength of a covalent bond is determined not only by the orbital overlap but also to a large degree by the *energy* of the valence electrons. A related, but less studied question concerns the strength and the overlap population of the partial π bond between a $p(\pi)$ acceptor and a $p(\pi)$ donor as found in CF_3^+ or BF_3 . In a theoretical study of Gobbi and Frenking² about the electronic structure of $C(NH_2)_3^+$ and related compounds, it was shown that the partial C–N double bond in the guanidinium cation is very important for the understanding of the properties of the guanidinium ion, although the high basicity of guanidinium is not solely caused by the Y-conjugation. A recent theoretical study of the silicon homologue $Si(NH_2)_3^+$ predicted that the silaguanidinium cation has about 40% of the resonance

stabilization of the guanidinium cation.³ A theoretical/experimental study of $C(XR)_3^+$ (X = O, S, Se, Te) compounds of Grützmacher, Glaser, and co-workers⁴ showed that the sulfur, selenium, and tellurium carbenium ions have nearly the same stabilization energy relative to CH_3^+ .

In a recent theoretical and experimental study of halomethyl cations of Olah et al.⁵ the calculated and observed ¹³C chemical shifts of CX_3^+ (X = Cl, Br, I) among other halomethyl cations have been reported. The authors showed that there is a linear correlation between the Pauling electronegativities of the halogens with the differences between the ¹³C chemical shifts of the CX_3^+ cations and the respective neutral molecule $H CX_3$. The correlation was taken as evidence that there is a decreasing order of back-donation: $Cl > Br > I$. The decreasing order of π back-donation was explained with the overlap between the $p(\pi)$ orbitals of carbon and the halogens, which was given in the order $2p(\pi)-3p(\pi) > 2p(\pi)-4p(\pi) > 2p(\pi)-5p(\pi)$.⁵

The suggestion of Olah et al.⁵ that the $p(\pi)$ back-donation decreases in the order $Cl > Br > I$ is mainly based on the linear correlation with the ¹³C-NMR shifts. A linear correlation does not say, however, whether the $p(\pi)$ population decreases or increases. Theoretical studies of NMR chemical shifts revealed

[†] Philipps-Universität Marburg.

[‡] ETH Zürich.

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

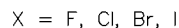
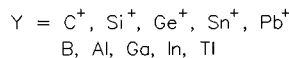
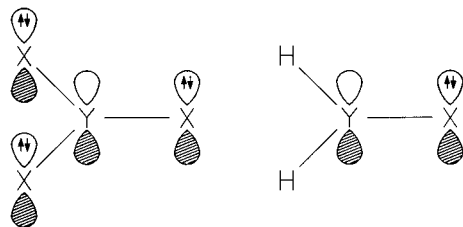
(1) (a) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (b) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

(2) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362.

(3) Pidun, U.; Stahl, M.; Frenking, G. *Chem. Eur. J.* **1996**, *2*, 869.

(4) Ohlmann, D.; Marchand, C. M.; Grützmacher, H.; Chen, G. S.; Farmer, D.; Glaser, R.; Currao, A.; Nesper, R.; Pritzkow, H. *Angew. Chem.* **1996**, *108*, 317; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 300.

(5) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580.

Scheme 1. Compounds Investigated in This Study

that the chemical shift is largely determined by the topology of the electron density distribution at the atom rather than by its partial charge.^{3,6} The conclusion of Olah et al.⁵ is in conflict with the results of earlier quantum chemical calculations of Bernardi et al.⁷ and conclusions which were made from gas-phase experiments.⁸ Also, it can be expected that the overlap population of the partial double bond $\text{X}_2\text{C}^+-\text{X} \leftrightarrow \text{X}_2\text{C}=\text{X}^+$ increases with $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$, because the positive charge makes the carbon atom a strong electron attractor, and the electronegativity of the halogens decreases from F to I.

After this study was completed, Schleyer and co-workers⁹ published a theoretical study about the stabilization of carbenium ions CH_2X^+ for various substituents X. In case of $\text{X} =$ halogen it was found that there is a regular increase in the stability of CH_2X^+ relative to CH_3^+ with $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$. It follows that the question about the π -donor ability of the halogen atoms (and other atoms with π -donor orbitals) in Y-conjugated molecules is unclear.

In this paper we address the following questions: (i) What is the order of π -back-donation of the halogens $\text{X} = \text{F, Cl, Br, I}$ in carbenium ions and heavy-atom homologues AX_3^+ ($\text{A} = \text{C, Si, Ge, Sn, Pb}$)? (ii) How does the order of π -back-donation relate to the thermodynamic stability of the cations? (iii) Which order of π -back-donation and thermodynamic stability is predicted for the singly substituted cations AH_2X^+ compared to triply substituted AX_3^+ ? (iv) Which order of π -back-donation and thermodynamic stability is predicted for the neutral isoelectronic compounds YX_3 and YH_2X ($\text{Y} = \text{B, Al, Ga, In, Tl}$)? In order to answer these questions, we optimized the geometries of AX_3^+ , AH_2X^+ , YX_3 , and YH_2X at the MP2 level of theory using valence basis sets of DZ+P quality. We also analyzed the electronic structure of the compounds using the NBO (natural bond orbital) method of Weinhold.¹⁰ The thermodynamic stability of the cations AX_3^+ and the neutral molecules YX_3 was estimated by calculating the complex formation energy of the water complexes $\text{X}_3\text{A}^+-\text{OH}_2$ and $\text{X}_3\text{Y}-\text{OH}_2$. Isoodesmic reaction energies are also given, which indicate for the cations the stabilization of the positive charge by substituting hydrogen for halogen and the differences of the hydride affinities of the neutral compounds.

Methods

The geometry optimization and the calculation of the vibrational frequencies were performed at the MP2 level of theory in the frozen-

core approximation. The following basis sets have been used. For H, C, O, and F a standard 6-31G(d) basis set¹¹ with five spherical d-functions for the polarization functions was employed. For the heavier atoms Si, Ge, Sn, and Pb and Cl, Br, and I a quasirelativistic pseudopotential has been used with a (31/31/1) valence basis set.¹² The valence basis sets for B, Al, Ga, In, and Tl have additional p-type functions leading to a 6-31/31/1 basis set for boron and valence basis sets (31/31/1) for Al, Ga, In, and Tl. The exponents for the d-type polarization functions are taken from Huzinaga.¹³ This basis set combination is denoted VDZ+P. Some energy calculations have been carried out with larger basis sets, which are augmented with diffuse functions. A 6-2111/2111/1 basis set was used for H, B, C, O, and F. The valence basis sets of the ECPs for Al, Ga, In, and Tl; Si, Ge, Sn, and Pb; and Cl, Br, and I have (2111/2111/1) quality, where the outermost s and p valence orbitals are diffuse functions. This basis set combination is denoted VTZ+D+P, where D stands for diffuse functions. Table 16 of the Supporting Information shows the basis sets used in this study.

All calculated structures reported in this paper are minima on the potential energy surface (all eigenvalues of the Hessian matrix are positive). The zero-point energies (ZPE) are scaled by 0.90. The calculations have been carried out using the program package Gaussian 94.¹⁴

Discussion

AX_3^+ ($\text{A} = \text{C, Si, Ge, Sn, Pb}$; $\text{X} = \text{F, Cl, Br, I}$). Table 1 shows the calculated A–X bond lengths of the cations AX_3^+ (D_{3h}) and the neutral molecules AHX_3 (C_{3v}). The A–X bonds are always significantly shorter in AX_3^+ than in AHX_3 . The bond shortening is similar for the A–Cl, A–Br, and A–I bonds of AX_3^+ for a given atom A, while it is less for the A–F bonds. The shortening of the A–X bonds of the carbenium ions is clearly higher than that of the heavier homologues $\text{A} = \text{Si, Ge, Sn, and Pb}$, where the bond length reduction is similar (Table 1). The change in the A–X bond lengths demonstrates the exceptional role of the elements of the first row of the periodic system.¹ Table 1 shows also the A–X and A–O interatomic distances of the $\text{X}_3\text{A}^+-\text{OH}_2$ complexes, which have C_s symmetry. The A–X bond lengths of $\text{X}_3\text{A}^+-\text{OH}_2$ are longer than in AX_3^+ , but remain shorter than in AHX_3 .

Table 2 shows the calculated partial charges and the $p(\pi)$ population at the central atom A of AX_3^+ cations. The $p(\pi)$ population at the carbon atom increases from CF_3^+ (0.60 e) to CCl_3^+ (0.91 e), CBr_3^+ (0.98 e), and CI_3^+ (1.05 e), i.e. $\text{F} < \text{Cl} < \text{Br} < \text{I}$, in contrast to what was suggested by Olah et al.⁵ The calculated charge distribution indicates that C^+ is a very powerful electron attractor in the heavier trihalogen carbenium ions. The carbon atom carries a positive charge of +1.55 in

(11) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

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

(13) Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatekawa, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam 1984.

(14) Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, I.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA 1995.

(15) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(16) (a) Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris, A. *J. Phys. Chem.* **1984**, *88*, 1950. (b) DeCorpo, J. J.; Bafus, D. A.; Franklin, J. L. *J. Chem. Thermodyn.* **1971**, *3*, 125.

(6) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR* **1990**, *23*, 165.

(7) Bernardi, F.; Bottoni, A.; Venturini, A. *J. Am. Chem. Soc.* **1986**, *108*, 5395.

(8) Taft, R. W.; Martin, R. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 2490.

(9) Kapp, J.; Schade, C.; El-Nahas, A. M.; Schleyer, P. v. R. *Angew. Chem.* **1996**, *108*, 2373; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236.

(10) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Table 1. Calculated (MP2/VDZ+P) Bond Lengths [Å] of AX₃⁺, AHX₃, and X₃A⁺-OH₂

A	X =				
	H	F	Cl	Br	I
	<i>r</i> _{A-X} of AX ₃ ⁺ (<i>D</i> _{3h})				
C	1.089	1.247	1.654	1.814	2.041
Si	1.482	1.554	1.975	2.137	2.367
Ge	1.530	1.677	2.070	2.225	2.447
Sn	1.696	1.840	2.244	2.397	2.617
Pb	1.731	1.916	2.336	2.490	2.708

A	X =				
	H ^a	F	Cl	Br	I
	<i>r</i> _{A-X} of AHX ₃ (<i>C</i> _{3v})				
C	1.090	1.345	1.775	1.937	2.167
Si	1.495	1.605	2.061	2.226	2.462
Ge	1.547	1.735	2.157	2.312	2.538
Sn	1.721	1.890	2.322	2.477	2.700
Pb	1.755	1.964	2.410	2.564	2.783

A	X =				
	H	F	Cl	Br	I
	<i>r</i> _{A-H}				
C	1.090	1.088	1.084	1.085	1.086
Si	1.495	1.476	1.482	1.485	1.489
Ge	1.547	1.526	1.533	1.538	1.543
Sn	1.721	1.697	1.701	1.706	1.712
Pb	1.755	1.726	1.736	1.744	1.753

A	X =				
	H	F	Cl	Br	I
	<i>r</i> _{A-H} ^b of X ₃ A ⁺ -OH ₂ (<i>C</i> _s)				
C	1.087/1.086	1.304/1.297	1.738/1.727	1.910/1.898	2.156/2.145
Si	1.481/1.479	1.569/1.572	2.010/2.005	2.175/2.169	2.411/2.404
Ge	1.529/1.527	1.691/1.696	2.100/2.095	2.257/2.251	2.484/2.478
Sn	1.697/1.695	1.849/1.853	2.259/2.265	2.414/2.420	2.636/2.643 ^c
Pb	1.730/1.728	1.921/1.924	2.346/2.351	2.504/2.509	2.725/2.730 ^c

A	X =				
	H	F	Cl	Br	I
	<i>r</i> _{A-O}				
C	1.519	1.551	1.598	1.602	1.596
Si	1.901	1.830	1.891	1.921	1.955
Ge	2.064	1.973	2.045	2.083	2.126
Sn	2.247	2.152	2.204	2.238	2.276
Pb	2.392	2.278	2.344	2.386	2.434

^a *T*_d. ^b First distance occurs once, second occurs twice. ^c C₁.

CF₃⁺, but it has a *negative* (!) charge in CCl₃⁺ (-0.17), CBr₃⁺ (-0.53), and CI₃⁺ (-0.90). This means that C⁺ is clearly more electronegative than chlorine. Chlorine, bromine, and iodine are *σ* and *π* donors in CX₃⁺. This becomes obvious by the calculated *σ* donation, which is given by the difference between the partial charges at X and the p(*π*) population at the carbon atom (Table 2).

The heavier central atoms Si, Ge, Sn, and Pb show the same trend in the p(*π*) population and charge distribution from X = F to I as CX₃⁺ (Table 2). The p(*π*) population of atom A in AX₃⁺ increases always from fluorine to iodine, but the absolute numbers are significantly lower than in the carbenium ions. All halogens are *σ* acceptors in SiX₃⁺-PbX₃⁺ with the trend F ≫ Cl > Br > I (Table 2). There is a regular decrease of the p(*π*) population C > Si > Ge > Sn > Pb for all halogen substituents. The heavier central atoms A always carry a positive partial charge in AX₃⁺, which becomes smaller from X = F to I (Table 2). The trend of the partial charges of the central atoms A for a given halogen is not regular. Si and Ge have similar charges in AX₃⁺ (X = Cl, Br, I), while the partial charges for A = Sn and Pb are clearly higher. It should be noted that the partial charges indicate the polarization of the *σ* and *π* bonds between A and X. The filling of the d-shell explains the similar charge of Ge and Si, while relativistic effects may be responsible for the slightly lower partial charge of Pb than Sn.

In order to estimate the thermodynamic stability of the Y-conjugated cations AX₃⁺, we calculated the methyl stabiliza-

Table 2. Results of the NBO Analysis of AX⁺ at MP2/VDZ+P

A	X =			
	F	Cl	Br	I
	Partial Charges <i>q</i> _A (<i>q</i> _X)			
C	1.55 (-0.18)	-0.17 (0.39)	-0.53 (0.51)	-0.90 (0.63)
Si	2.64 (-0.55)	1.54 (-0.18)	1.15 (-0.05)	0.58 (0.14)
Ge	2.52 (-0.51)	1.57 (-0.19)	1.20 (-0.07)	0.65 (0.12)
Sn	2.70 (-0.57)	1.97 (-0.32)	1.61 (-0.20)	1.09 (-0.03)
Pb	2.49 (-0.50)	1.88 (-0.29)	1.54 (-0.18)	1.07 (-0.02)

A	p(<i>π</i>) Population at A			
	F	Cl	Br	I
C	0.60	0.91	0.98	1.05
Si	0.26	0.44	0.52	0.63
Ge	0.23	0.38	0.46	0.57
Sn	0.18	0.28	0.35	0.45
Pb	0.16	0.23	0.30	0.38

A	Total <i>σ</i> Donation from A to X ₃ ^a			
	F	Cl	Br	I
C	1.15	-0.26	-0.55	-0.85
Si	1.90	0.98	0.67	0.21
Ge	1.75	0.95	0.66	0.22
Sn	1.88	1.25	0.96	0.54
Pb	1.65	1.11	0.84	0.45

^a Calculated from the difference between the sum of partial charges at X and the p(*π*) population at A. Positive numbers give *σ* donation A → X₃, negative numbers give *σ* donation X₃ → A.

tion energies (MSE) given by the isodesmic reaction 1:

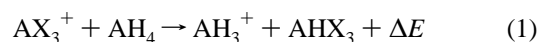


Table 3 shows the theoretically predicted energies for reaction 1, which are in good agreement with experimentally derived values. Positive values for *ΔE* mean that X stabilizes the cation relative to AH₃⁺, while negative values indicate destabilization. We calculated also the complex formation energies of the complexes X₃A⁺-OH₂, which may additionally be used to estimate the stabilization of the positive charge by the substituent X. The bond energies of the water complexes are shown in Table 4.

Table 3 shows that all halogens stabilize the carbenium ions CX₃⁺ relative to CH₃⁺. Even fluorine has a stabilizing effect due to its p(*π*) donation, although the total *σ* + *π* effect leads to a more positive charge at the carbon atom. *This demonstrates the particular role of the π donation for the stabilization of cations.* The MSE values increase strongly from fluorine to chlorine, because chlorine is a *σ* and a *π* donor. Figure 1 shows a plot of the calculated energies for reaction 1, which illustrates the trend of the MSE values. There is an increase in the stabilization of CX₃⁺ with F < Cl < Br < I. The same trend is found for the MSE values of the heavier homologues SiX₃⁺-PbX₃⁺. However, the halogens do not always stabilize the cations. F and Cl destabilize SiX₃⁺, while Br and I stabilize the silicenium ion. Iodine has a stabilizing effect in GeI₃⁺ and SnI₃⁺, while the other halogens destabilize GeX₃⁺ and SnX₃⁺. All halogens destabilize PbX₃⁺. It follows that the stabilizing effect of the halogens in AX₃⁺ is weaker and may become destabilizing when the halogen becomes more electronegative and the central atom becomes more electropositive. The MSE energies show the same trend as the p(*π*) population of A in AX₃⁺.

The calculated complex formation energies of X₃A⁺-OH₂ (Table 4) show very interesting trends, which are displayed in Figure 2. The complexation energy of F₃C⁺-OH₂ is *lower* than that calculated for H₃C⁺-OH₂, while the trifluorides of the heavier atoms F₃A⁺ (A = Si, Ge, Sn, Pb) form *stronger* bonded water complexes than H₃A⁺. This is in agreement with the calculated reaction energies for the isodesmic reaction 1 (Table 3) which show that fluorine stabilizes the carbenium ion CF₃⁺

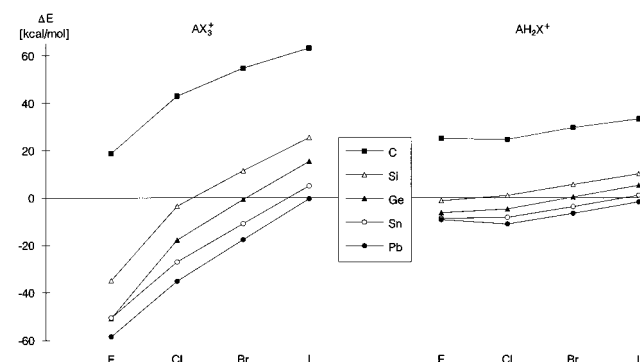
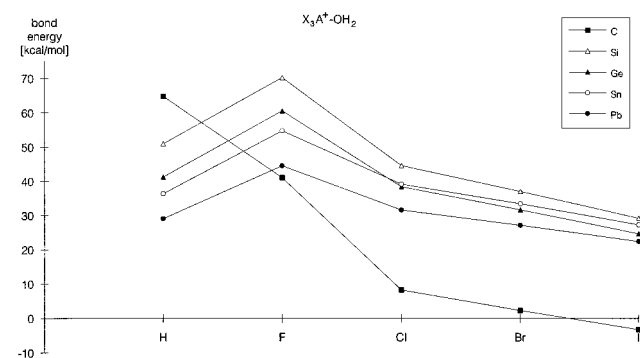
Table 3. Calculated (MP2/VDZ+P) Reaction Energies [kcal/mol] of the Isodesmic Reaction 1 with Values Including Scaled ZPE's in Parentheses and Experimental Values^a in Italics

A	X =									
	F		Cl		Br		I			
C	18.8	(17.4)	<i>17.7</i>	42.9	(41.8)	<i>44.1^b</i>	54.7	(53.6)	63.1	(62.0)
Si	-34.9	(-35.2)	<i>-33.9</i>	-3.6	(-4.0)	<i>-6.1</i>	11.5	(11.1)	25.5	(25.0)
Ge	-50.8	(-51.0)		-17.8	(-18.2)		-0.7	(-1.0)	15.4	(15.1)
Sn	-50.5	(-50.6)		-27.1	(-27.3)		-10.8	(-11.1)	5.1	(4.8)
Pb	-58.5	(-58.5)		-35.2	(-35.5)		-17.6	(-17.9)	-0.4	(-0.7)

^a Reference 15. ^b Taken from ref 15 with use of the experimental ionization energy of CCl₃.

Table 4. Calculated (MP2/VTZ+D+P) Bond Energies [kcal/mol] of X₃A⁺-OH₂ with Values Including Scaled ZPE's (MP2/VDZ+P) in Parentheses

A	X =									
	H	F	Cl	Br	I					
C	71.3 (64.8)	43.7 (41.1)	10.9 (8.3)	4.9 (2.3)	-0.6 (-3.2)					
Si	54.7 (51.0)	72.4 (70.3)	46.8 (44.6)	39.2 (37.0)	31.3 (29.2)					
Ge	44.5 (41.2)	62.7 (60.6)	40.4 (38.4)	33.6 (31.7)	26.6 (24.7)					
Sn	38.9 (36.3)	56.7 (54.8)	40.8 (39.2)	35.0 (33.4)	28.9 (27.3)					
Pb	31.4 (29.0)	46.4 (44.5)	33.2 (31.6)	28.6 (27.1)	23.8 (22.4)					

**Figure 1.** Plot of the calculated energies for the isodesmic reaction 1 of AX₃⁺ (left) and for reaction 2 of AH₂X⁺ (right) (A = C, Si, Ge, Sn, Pb).**Figure 2.** Plot of the calculated bond energies X₃A⁺-OH₂ (A = C, Si, Ge, Sn, Pb).

with respect to CH₃⁺, while the heavier homologues AF₃⁺ are destabilized relative to AH₃⁺. There is a regular decrease of the halogen substituted X₃A⁺-OH₂ bond energies for each central atom A with X = F > Cl > Br > I. The calculations with the larger VTZ+D+P basis set even predict that I₃C⁺-OH₂ is not a stable complex. This is a further indication that the heavier halogen atoms stabilize the cations AX₃⁺ more than the lighter halogens.

The trend for the central atoms A taken from the complex bond energies of the halogen substituted species shows that silicon has the strongest bond. This means that silicenium ions SiX₃⁺ are the least stable species among the isoelectronic AX₃⁺

Table 5. Calculated (MP2/VDZ+P) Bond Lengths [Å] of AH₂X⁺ and AH₃X

A	X =				
	H ^a	F	Cl	Br	I
<i>r</i> _{A-X} of AH ₂ X ⁺ (C _{2v})					
C	1.089	1.245	1.603	1.739	1.940
Si	1.482	1.570	1.976	2.123	2.335
Ge	1.530	1.701	2.075	2.211	2.414
Sn	1.696	1.863	2.256	2.394	2.595
Pb	1.731	1.940	2.344	2.479	2.675
<i>r</i> _{A-H}					
C	1.089	1.091	1.089	1.089	1.088
Si	1.482	1.481	1.482	1.484	1.485
Ge	1.530	1.530	1.531	1.532	1.534
Sn	1.696	1.694	1.696	1.697	1.700
Pb	1.731	1.725	1.728	1.731	1.736
A	X =				
	H ^b	F	Cl	Br	I
<i>r</i> _{A-X} of AH ₃ X (C _{3v})					
C	1.090	1.393	1.801	1.947	2.158
Si	1.495	1.632	2.094	2.251	2.476
Ge	1.547	1.772	2.200	2.344	2.557
Sn	1.721	1.925	2.370	2.513	2.725
Pb	1.755	2.010	2.470	2.608	2.811
<i>r</i> _{A-H}					
C	1.090	1.092	1.087	1.087	1.087
Si	1.495	1.494	1.490	1.491	1.491
Ge	1.547	1.546	1.541	1.542	1.542
Sn	1.721	1.717	1.712	1.714	1.715
Pb	1.755	1.750	1.744	1.746	1.748

^a D_{3h}. ^b T_d.

cations. The search for a stable silicenium ion in a condensed phase is a topic of ongoing experimental and theoretical research.^{3,17} The results shown in Table 4 indicate that it should be easier to synthesize the heavier homologues GeX₃⁺, SnX₃⁺, and particularly PbX₃⁺ than SiX₃⁺.

We want to emphasize that the opposite trend of the π -donor ability of the halogens which is found in our investigation does not affect the value of the experimental results reported by Olah et al.⁵ The theoretical analysis given here shows that the linear correlation of ¹³C-NMR chemical shifts with Pauling's electronegativities, which led to the suggestion that the p(π) back-donation of the heavier halogens becomes smaller, is fortuitous.

AH₂X⁺ (A = C, Si, Ge, Sn, Pb; X = F, Cl, Br, I). Table 5 shows the theoretically predicted A-X bond lengths of the cations AH₂X⁺ and the neutral compounds AH₃X. As expected, the A-X bonds of the cations are shorter than in the neutral molecules. A comparison of the calculated bond lengths (Table 1) shows that the C-X bonds of the singly substituted

(17) (a) Olah, G. A.; Rasul, G.; Buchholz, H. A.; Li, X.-Y.; Prakash, G. K. S. *Bull. Soc. Chim. Fr.* **1995**, 132, 569. (b) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, 95, 1191. (c) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, 117, 7460. (d) Olah, G. A.; Rasul, G.; Li, X.-Y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, 263, 983.

Table 6. Results of the NBO Analysis of AH_2X^+ at MP2/VDZ+P

A	X =			
	F	Cl	Br	I
Partial Charges q_A (q_X)				
C	0.66 (-0.14)	-0.05 (0.48)	-0.24 (0.66)	-0.45 (0.87)
Si	1.87 (-0.56)	1.45 (-0.20)	1.30 (-0.06)	1.10 (0.14)
Ge	1.78 (-0.54)	1.42 (-0.22)	1.29 (-0.09)	1.09 (0.10)
Sn	2.02 (-0.59)	1.74 (-0.36)	1.62 (-0.24)	1.44 (-0.07)
Pb	1.87 (-0.57)	1.63 (-0.37)	1.52 (-0.25)	1.35 (-0.08)
$p(\pi)$ Population at A				
C	0.31	0.52	0.60	0.69
Si	0.12	0.19	0.23	0.29
Ge	0.11	0.17	0.21	0.26
Sn	0.09	0.12	0.15	0.20
Pb	0.09	0.11	0.14	0.18
σ Donation from A to X^a				
C	0.45	0.04	-0.06	-0.18
Si	0.68	0.39	0.29	0.15
Ge	0.65	0.39	0.30	0.16
Sn	0.68	0.48	0.39	0.27
Pb	0.66	0.48	0.39	0.26

^a Calculated from the difference between the partial charge at X and the $p(\pi)$ population at A. Positive numbers give σ donation $\text{A} \rightarrow \text{X}$, negative numbers give σ donation $\text{X} \rightarrow \text{A}$.

carbenium cations CH_2X^+ are always *shorter* than in the triply substituted cations CX_3^+ . In particular the C–I bond is clearly shorter (1.940 Å) in CH_2I^+ than in Cl_3^+ (2.041 Å). This is an interesting result, particularly because the C–X bonds of neutral CH_3X are *longer* (with exception of CH_3I) than those in CHX_3 (Tables 1 and 5). The A–X bonds of the heavier homologues AH_2X^+ (A = Si, Ge, Sn, Pb) are always *longer* than those in AX_3^+ .

Table 6 shows the results of the NBO analysis of AH_2X^+ . The $p(\pi)$ population at atom A has about half the size in the singly substituted cations AH_2X^+ as in AX_3^+ (Tables 2 and 6). The trend of the $\text{X} \rightarrow \text{A}$ $p(\pi)$ donation for the halogens in AH_2X^+ is the same as that in AX_3^+ : $\text{F} < \text{Cl} < \text{Br} < \text{I}$. The $p(\pi)$ donation to the heavier atoms Si to Pb is clearly lower than what is calculated for carbon. Si and Ge have similar $p(\pi)$ donation, which is slightly higher than predicted for Sn and Pb. The $\text{A} \rightarrow \text{X}$ σ donation is also significantly lower in AH_2X^+ than in AX_3^+ . Carbon is a weak $\text{C} \rightarrow \text{Cl}$ σ donor in CH_2Cl^+ , but it is a σ acceptor in CH_2Br^+ and CH_2I^+ . It is interesting to note that the σ donation $\text{A} \rightarrow \text{F}$ for A = Si to Pb is nearly constant (Table 6). The $\text{A} \rightarrow \text{X}$ donation of the heavier atoms A is clearly higher than for carbon, and the values for the chlorides, bromides, and iodides of Si and Ge on the one hand and Sn and Pb on the other hand are very similar.

The atomic partial charges at the central atom A of AH_2X^+ become less positive or even negative from X = F to I, but the changes are less than for AX_3^+ (Tables 2 and 6). A comparison of the partial charges between AH_2X^+ and AX_3^+ is interesting. The carbon atom has less positive charge in CH_2F^+ when compared to CF_3^+ . On the other hand, it is less negatively charged in the heavier homologues CH_2X^+ (X = Cl, Br, I) than in the corresponding CX_3^+ ions (Tables 2 and 6). The situation is more complicated for the Si, Ge, Sn, and Pb homologues of AH_2X^+ . For X = F and Cl, the positive charges at the central atom are lower than in AX_3^+ , while $q(\text{A})$ is clearly higher when X = I. Similar partial charges are calculated for AH_2Br^+ and ABr_3^+ (A = Si, Ge, Sn, Pb). Relativistic effects and the filling of the d-shell make the trends in the partial charges less regular, while they appear to have little influence on the trend of the σ and π donation.

We calculated the MSE of AH_2X^+ for the isodesmic reaction 2:

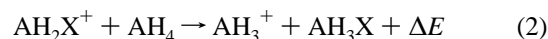


Table 7 shows the theoretically predicted stabilization energies for reaction 2. Figure 1 shows the trend of the calculated reaction energies of AH_2X^+ (reaction 2) in comparison with the calculated trend for AX_3^+ (reaction 1). While the absolute numbers of the MSE values for reaction 2 are clearly different from reaction 1 (Tables 3 and 7), the trends are similar and yet show notable differences. Generally, the alteration from fluorine to iodine is much less in the monohalogen cations AH_2X^+ than in the trihalogen cations AX_3^+ . The MSEs of chlorine and fluorine in AH_2X^+ are very similar, while the MSE of chlorine is much higher (or less destabilizing) than that of fluorine in AX_3^+ . Particularly noteworthy is the role of the halogens upon the stabilization of the carbenium ions in CH_2X^+ compared to CX_3^+ . Fluorine stabilizes CH_2F^+ more than CF_3^+ , although the $\text{F} \rightarrow \text{C}$ $p(\pi)$ donation is higher in CF_3^+ than in CH_2F^+ , while the stabilization of Cl, Br, and I is clearly higher in CX_3^+ than in CH_2X^+ . A comparison of the trends exhibited in Figure 1 shows clearly that fluorine has a particularly destabilizing effect (less stabilizing in the case of CF_3^+) in the AF_3^+ cations compared to AH_2F^+ . This can be explained by the strong σ -withdrawing effect of fluorine, which leads to a much higher positive charge at the central atoms A in AF_3^+ than in AH_2F^+ (compare the partial charges shown in Tables 2 and 6).

A comparison of the trends of the MSE values for AH_2X^+ and AX_3^+ shown in Figure 1 makes it clear that the stabilizing effect of the halogen substituents in AX_3^+ cannot be deduced from the stabilizing effect of one halogen in AH_2X^+ . The effect of multiple substitution of hydrogen by a halogen upon the stability of AX_3^+ is not additive! In particular, the thermodynamic stabilization of a cation *cannot* be deduced from the strength of the π donation of a substituent alone as stated by some authors.¹⁸ The trends exhibited in Figures 1 and 2 indicate clearly the difference between the carbenium ions CX_3^+ and CH_2X^+ and the heavier homologues AX_3^+ and AH_2X^+ (A = Si, Ge, Sn, Pb).

YX₃ (Y = B, Al, Ga, In, Tl; X = F, Cl, Br, I). Table 8 shows the theoretically predicted Y–X bond lengths of the Lewis acids YX_3 , which are in good agreement with experimental values. Table 8 also shows the Y–X interatomic distances of the water complexes $\text{X}_3\text{Y}-\text{OH}_2$ and the hydrides YHX_3^- . The Y–X bond lengths of the water complexes $\text{X}_3\text{Y}-\text{OH}_2$ are slightly longer than in YX_3 , while they are significantly longer in YHX_3^- .

Table 9 shows the results of the NBO analysis. The $p(\pi)$ population is always lower at the central atom of YX_3 than in the isoelectronic AX_3^+ cation, but the trend is the same. There is a regular increase from F to I and a decrease from B to Tl, except for TlCl_3 which has a slightly lower $p(\pi)$ population than TlF_3 . It follows that the trend of the $p(\pi)$ donation $\text{F} < \text{Cl} < \text{Br} < \text{I}$ is virtually the same in cations and neutral compounds. The atomic partial charges at the central atoms of the neutral fluorides are less positive than for the central atoms of AF_3^+ (Table 9). The trend of the partial charges at the metal shows that the positive charge decreases always from the fluorides to the chlorides, bromines, and iodines, but the trend for a given halogen is not regular. The metal fluoride with the most positively charged central atom is AlF_3 , while the highest positive charge at the central atom of the metal chlorides, bromides, and iodides is in InX_3 . All metal trihalogenides YX_3 show a $\text{Y} \rightarrow \text{X}$ σ donation, which decreases with $\text{X} = \text{F} > \text{Cl} > \text{Br} > \text{I}$.

(18) Apeloig, Y.; Karni, M. *J. Chem. Soc., Perkin Trans. 2* **1988**, 625.
(b) Hevesi, L. *Phosphorus Sulfur* **1988**, 38, 191.

Table 7. Calculated (MP2/VDZ+P) Reaction Energies [kcal/mol] of the Isodesmic Reaction 2 with Values Including Scaled ZPE's in Parentheses and Experimental Values^a in Italics

A	X =											
	F		Cl		Br		I					
C	25.1	(24.4)	<i>21.1</i>	24.8	(24.3)	<i>26.7^b</i>	29.8	(29.4)	<i>29.0^c</i>	33.5	(33.1)	<i>37^d</i>
Si	-1.2	(-1.2)		1.1	(1.1)		5.7	(5.7)		10.3	(10.2)	
Ge	-6.3	(-6.2)		-4.6	(-4.6)		0.4	(0.5)		5.4	(5.5)	
Sn	-8.6	(-8.5)		-8.2	(-8.1)		-3.6	(-3.5)		1.2	(1.3)	
Pb	-9.2	(-9.1)		-11.0	(-10.9)		-6.5	(-6.3)		-1.6	(-1.5)	

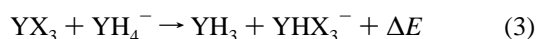
^a Reference 15. ^b Taken from ref 15 with use of the experimental ionization energy of CH₂Cl. ^c Taken from ref 15 with use of the experimental ionization energy of CH₂Br. ^d Reference 16.

Table 8. Calculated (MP2/VDZ+P) Bond Lengths [Å] of YX₃, X₃Y-OH₂ and YHX₃⁻

Y	X =				
	H	F	Cl	Br	I
<i>r_{Y-X} of YX₃ (D_{3h})</i>					
B	1.191	1.325	1.744	1.901	2.128
Al	1.597	1.641	2.083	2.246	2.479
Ga	1.587	1.739	2.135	2.284	2.504
In	1.750	1.866	2.284	2.431	2.651
Tl	1.743	1.806	2.338	2.495	2.710
<i>r_{Y-X} of X₃Y-OH₂ (C_s)</i>					
B	1.208/1.202	1.350/1.365	1.823/1.803	1.993/1.968	2.232/2.205
Al	1.604/1.614	1.652/1.661	2.105/2.124	2.269/2.291	2.504/2.529
Ga	1.590/1.602	1.750/1.763	2.152/2.172	2.301/2.324	2.522/2.548
In	1.754/1.765	1.873/1.886	2.297/2.314	2.444/2.464	2.664/2.687
Tl	1.741/1.752	1.811/1.832	2.346/2.368	2.501/2.524	2.716/2.740
<i>r_{Y-O}</i>					
B	1.734	1.791	1.673	1.661	1.652
Al	2.078	1.997	1.989	1.999	2.011
Ga	2.278	2.125	2.136	2.157	2.180
In	2.348	2.235	2.230	2.246	2.264
Tl	2.608	2.413	2.397	2.430	2.470
Y	X =				
	H ^b	F	Cl	Br	I
<i>r_{Y-X} of YHX₃⁻ (C_{3v})</i>					
B	1.239	1.432	1.885	2.046	2.275
Al	1.662	1.700	2.196	2.367	2.607
Ga	1.667	1.819	2.261	2.415	2.640
In	1.825	1.931	2.392	2.546	2.775
Tl	1.824	1.931	2.479	2.634	2.850
<i>r_{Y-H}</i>					
B	1.239	1.232	1.195	1.191	1.188
Al	1.662	1.640	1.601	1.600	1.599
Ga	1.667	1.621	1.581	1.584	1.585
In	1.825	1.792	1.750	1.752	1.753
Tl	1.824	1.780	1.721	1.727	1.733

^a First distance occurs once, second occurs twice. ^b T_d.

We studied theoretically the effect of the halogens upon the Lewis acidity of YX₃. The reader should be reminded that the absolute *and* the relative Lewis acidity depends on the nature of the Lewis base, which is chosen as a bonding partner for the donor-acceptor complex. For example, BCl₃ forms stronger bonded complexes than BF₃ with the strong Lewis bases NH₃ and NMe₃, while the weak Lewis bases CO and MeCN form stronger bonds with BF₃ than with BCl₃.¹⁹ In the present case, we calculated the reaction energy of isodesmic reaction 3, which gives the difference in the hydride affinity of YX₃ and YH₃:



The calculated reaction energies for reaction 3 are given in Table 10. The trends of the relative hydride affinities are shown

(19) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

Table 9. Results of the NBO Analysis of YX₃ at MP2/VDZ+P

Y	X =			
	F	Cl	Br	I
Partial Charges <i>q_Y</i> (<i>q_X</i>)				
B	1.48 (-0.49)	0.28 (-0.09)	-0.03 (0.01)	-0.45 (0.15)
Al	2.09 (-0.70)	1.52 (-0.51)	1.29 (-0.43)	0.89 (-0.30)
Ga	1.94 (-0.65)	1.43 (-0.48)	1.17 (-0.39)	0.74 (-0.25)
In	2.05 (-0.68)	1.66 (-0.55)	1.41 (-0.47)	1.04 (-0.35)
Tl	1.99 (-0.66)	1.56 (-0.52)	1.31 (-0.44)	0.94 (-0.31)
p(π) Population at Y				
B	0.34	0.50	0.54	0.59
Al	0.17	0.22	0.26	0.32
Ga	0.16	0.20	0.25	0.31
In	0.14	0.16	0.20	0.25
Tl	0.14	0.13	0.17	0.22
Total σ Donation from Y to X ₃ ^a				
B	1.82	0.78	0.51	0.14
Al	2.26	1.74	1.55	1.21
Ga	2.10	1.63	1.42	1.05
In	2.19	1.82	1.61	1.29
Tl	2.13	1.69	1.48	1.16

^a Calculated from the difference between the sum of partial charges at X and the p(π) population at Y. Positive numbers give σ donation Y \rightarrow X₃, negative numbers give σ donation X₃ \rightarrow Y.

Table 10. Calculated (MP2/VTZ+D+P) Reaction Energies [kcal/mol] of the Isodesmic Reaction 3 with Values Including Scaled ZPE's (MP2/VDZ+P) in Parentheses

Y	X =							
	F		Cl		Br		I	
B	-6.7	(-6.2)	-28.9	(-28.0)	-35.1	(-34.0)	-44.2	(-43.0)
Al	-27.0	(-26.6)	-33.8	(-33.2)	-34.0	(-33.4)	-36.6	(-35.9)
Ga	-43.7	(-42.9)	-44.7	(-43.8)	-42.9	(-41.9)	-43.0	(-42.0)
In	-39.7	(-38.9)	-42.8	(-42.1)	-41.1	(-40.3)	-40.4	(-39.6)
Tl	-43.2	(-42.3)	-54.2	(-53.4)	-50.9	(-50.0)	-48.2	(-47.3)

in Figure 3. All halogens *increase* the hydride affinity of YX₃ relative to YH₃. The boron halides show for the hydride affinity the order BH₃ < BF₃ \ll BCl₃ < BBr₃ < BI₃. The trends calculated for the heavier homologues of the boron halides are less regular. The fluorides YF₃ (Y = Al, Ga, In, Tl) have a significantly larger hydride affinity than YH₃, but the hydride affinity does not change much when fluorine is substituted by heavier halogens. GaX₃ and InX₃ are predicted to have nearly the same hydride affinity for X = F, Cl, Br, I, while Tl shows a rather large difference between TlF₃ and TlCl₃.

We calculated the bond energies of the water complexes X₃Y-OH₂. The results are shown in Table 11. Figure 4 displays the trend of the calculated complexation energies with water. The trend of the calculated bond energies ΔE is very different from the trend of the hydride affinities shown in Figure 3. The bond energies of the boron complexes X₃B-OH₂ change very little from X = F (ΔE = 11.0 kcal/mol) to I (ΔE = 9.8 kcal/mol), and they are slightly lower than for H₃B-OH₂ (ΔE

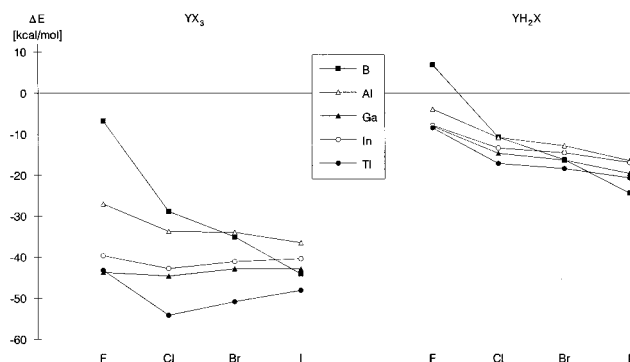


Figure 3. Plot of the calculated energies for the isodesmic reaction 3 of YX_3 (left) and for reaction 4 of YH_2X (right) ($Y = B, Al, Ga, In, Tl$).

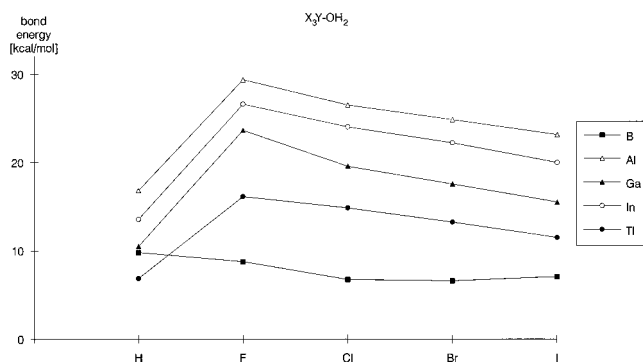


Figure 4. Plot of the calculated bond energies X_3Y-OH_2 ($Y = B, Al, Ga, In, Tl$).

Table 11. Calculated (MP2/VTZ+D+P) Bond Energies [kcal/mol] of X_3Y-OH_2 with Values Including Scaled ZPE's (MP2/VDZ+P) in Parentheses

Y	X =				
	H	F	Cl	Br	I
B	14.3 (9.8)	11.0 (8.7)	9.5 (6.7)	9.3 (6.6)	9.8 (7.0)
Al	19.8 (16.8)	31.9 (29.4)	28.8 (26.5)	27.1 (24.9)	25.3 (23.2)
Ga	13.1 (10.5)	26.0 (23.6)	21.7 (19.6)	19.6 (17.6)	17.5 (15.5)
In	16.0 (13.5)	28.8 (26.6)	26.1 (24.0)	24.2 (22.2)	22.0 (20.0)
Tl	8.9 (6.8)	18.1 (16.1)	16.7 (14.8)	15.0 (13.2)	13.2 (11.5)

= 14.3 kcal/mol). It follows that the halogens increase the hydride affinity of BX_3 relative to BH_3 , while they reduce the affinity toward water. There seems to be a cancellation of two opposite effects, which is responsible for the similar complexation energies of the boron trihalides with H_2O . One effect is the strength of the partial B–X double bond, which decreases from fluorine to iodine. The second effect is the $p(\pi)$ population and the partial charge at boron. The second effect supports the X_3B-OH_2 bond for the lighter halogens, while the weaker partial B–X π bond enhances the complex formation for the heavier halogens.

The strongest complexation energies of the water complexes X_3Y-OH_2 are calculated for $Y = Al$ (Table 11). This is in agreement with the experimentally determined bond strength of main-group donor–acceptor complexes.² The strongest bonded complex that is known is $Cl_3Al-NMe_3$, which is stronger bound than Cl_3B-NMe_3 .^{2,20} The calculated water affinity of the trihalogenides X_3Y shows the order $Al > In > Ga > Tl > B$. All trihalogenides of the heavier elements Al to Tl have a significantly stronger bond to water than the hydrides, while the boron trihalogenides have a lower water affinity than

Table 12. Calculated (MP2/VDZ+P) Bond Lengths [Å] of YH_2X and YH_3X^-

Y	X =				
	H ^a	F	Cl	Br	I
	r_{Y-X} of YH_2X (C_{2v})				
B	1.191	1.335	1.750	1.899	2.117
Al	1.597	1.656	2.117	2.276	2.503
Ga	1.587	1.773	2.187	2.326	2.536
In	1.750	1.894	2.333	2.472	2.684
Tl	1.743	1.866	2.425	2.564	2.763
	r_{Y-H}				
B	1.191	1.192	1.187	1.187	1.186
Al	1.597	1.590	1.586	1.587	1.588
Ga	1.587	1.574	1.569	1.571	1.573
In	1.750	1.739	1.731	1.733	1.735
Tl	1.743	1.727	1.711	1.714	1.718
Y	X =				
	H ^b	F	Cl	Br	I
	r_{Y-X} of YH_3X^- (C_{3v})				
B	1.239	1.466	1.991	2.163	2.411
Al	1.662	1.713	2.276	2.455	2.710
Ga	1.667	1.856	2.382	2.543	2.783
In	1.825	1.959	2.487	2.648	2.893
Tl	1.824	2.000	2.653	2.807	3.033
	r_{Y-H}				
B	1.239	1.247	1.219	1.215	1.211
Al	1.662	1.663	1.638	1.636	1.632
Ga	1.667	1.663	1.631	1.629	1.624
In	1.825	1.825	1.795	1.794	1.790
Tl	1.824	1.820	1.779	1.779	1.777

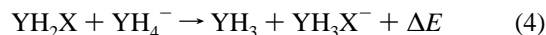
^a D_{3h} . ^b T_d .

BH_3 . The calculated stabilization energies for reaction 3 and for the bond energies of the water complexes show that no single parameter of the electronic structure, i.e. atomic charge, $p(\pi)$ donation, or σ donation, is the dominant factor that determines the bond strength of the Lewis acids with a nucleophile. This is not surprising, because the very different trends for the hydride affinity and the water affinity show that the attractive interactions depend strongly on the nature of the nucleophile.

YH_2X ($Y = B, Al, Ga, In, Tl$; $X = F, Cl, Br, I$). Table 12 shows the calculated bond lengths of the neutral compounds YH_2X and the hydrides YH_3X^- . The Y–X bonds of YH_2X are longer than in YX_3 , with the notable exceptions of BH_2I and BH_2Br , which has nearly the same B–Br distance as BBR_3 . The Y–X bonds and the Y–H bonds become much longer in the hydrides YH_3X^- . The Y–X bonds of YH_3X^- are always longer than those in YHX_3^- (Tables 8 and 12). This is a hint that YH_2X has a lower Lewis acidity (more exact: hydride affinity) than YX_3 .

Table 13 shows the results of the NBO analysis. Like the isoelectronic cations, the $p(\pi)$ population is clearly lower at the central atom Y of YH_2X^+ than in YX_3 (Tables 9 and 13). The $p(\pi)$ population at atom Y does not change significantly from F to I. The boron trihalogenides have a larger $p(\pi)$ population and a lower $Y \rightarrow X$ σ donation than the heavy-atom homologues, which have similar $p(\pi)$ values and $Y \rightarrow X$ σ donation for each of the halogens. The central atoms of YH_2X are always positively charged (Table 13). Boron carries a smaller positive charge than the heavier central atoms, which exhibit an irregular trend for the partial charges.

Table 14 shows the calculated energies for the isodesmic reaction 4, which gives the difference between the hydride affinity of YH_2X and YH_3 :



(20) Haaland, A. *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

Table 13. Results of the NBO Analysis of YH_2X at MP2/VDZ+P

Y	X =							
	F		Cl		Br		I	
Partial Charges q_Y (q_X)								
B	0.76	(-0.48)	0.32	(-0.17)	0.22	(-0.09)	0.11	(0.01)
Al	1.56	(-0.70)	1.34	(-0.55)	1.26	(-0.49)	1.15	(-0.39)
Ga	1.37	(-0.66)	1.18	(-0.54)	1.10	(-0.48)	0.98	(-0.37)
In	1.47	(-0.68)	1.31	(-0.61)	1.23	(-0.54)	1.12	(-0.44)
Tl	1.36	(-0.67)	1.22	(-0.62)	1.14	(-0.55)	1.03	(-0.45)
$p(\pi)$ Population at Y								
B	0.16		0.18		0.19		0.20	
Al	0.08		0.08		0.09		0.10	
Ga	0.08		0.07		0.08		0.10	
In	0.07		0.06		0.07		0.08	
Tl	0.07		0.05		0.06		0.08	
σ Donation from Y to X^a								
B	0.64		0.35		0.28		0.19	
Al	0.78		0.63		0.58		0.49	
Ga	0.74		0.61		0.56		0.47	
In	0.75		0.67		0.61		0.52	
Tl	0.74		0.67		0.61		0.53	

^a Calculated from the difference between the partial charge at X and the $p(\pi)$ population at Y. Positive numbers give σ donation $\text{Y} \rightarrow \text{X}$, negative numbers give σ donation $\text{X} \rightarrow \text{Y}$.

Table 14. Calculated (MP2/VTZ+D+P) Reaction Energies [kcal/mol] of the Isodesmic Reaction 4 with Values Including Scaled ZPE's (MP2/VDZ+P) in Parentheses

Y	X =							
	F		Cl		Br		I	
B	6.8	(6.7)	-10.7	(-10.2)	-16.3	(-15.6)	-24.4	(-23.7)
Al	-4.0	(-3.9)	-10.8	(-10.5)	-12.8	(-12.5)	-16.5	(-16.1)
Ga	-8.1	(-7.9)	-14.7	(-14.2)	-16.3	(-15.8)	-19.6	(-19.0)
In	-7.9	(-7.6)	-13.4	(-13.0)	-14.6	(-14.1)	-16.9	(-16.5)
Tl	-8.5	(-8.3)	-17.2	(-16.8)	-18.4	(-18.0)	-20.7	(-20.2)

The trend of the calculated energies for reaction 4 is displayed in Figure 3, which also shows the trend for relative hydride affinities of YX_3 . The hydride affinity of YH_2X increases slightly with $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$. BH_2F has a lower hydride affinity than BH_3 , while the other metal halogenides have higher hydride affinities than YH_3 . The absolute values are lower for the hydride affinity of YH_2X than for YX_3 (Tables 10 and 14). *The hydride affinity of YH_2X and YX_3 does not correlate with the $p(\pi)$ population or atomic partial charge of Y!* Figures 3 and 4 indicate clearly the difference between the boron compounds and the heavier homologues YX_3 and YH_2X ($\text{Y} = \text{Al, Ga, In, Tl}$).

Summary

The calculated $p(\pi)$ population of the atoms bonded to a halogen shows that the π donor ability of the halogens increases with $\text{F} < \text{Cl} < \text{Br} < \text{I}$ in the cations AX_3^+ and AH_2X^+ and in the neutral molecules YX_3 ($\text{A} = \text{C, Si, Ge, Sn, Pb}$; $\text{Y} = \text{B, Al, Ga, In, Tl}$; $\text{X} = \text{F, Cl, Br, I}$). The neutral compounds YH_2X , however, show little differences in the $p(\pi)$ population at Y

from $\text{X} = \text{fluorine to iodine}$. C^+ and boron are significantly stronger π acceptors than the heavier homologues Si^+ to Pb^+ and Al to Tl , respectively. The calculated energies of isodesmic reactions predict that the stabilizing effect of the halogens in the carbenium ions CX_3^+ increases strongly from fluorine to chlorine. Carbon is a strong π acceptor in CX_3^+ and even a σ acceptor in CCl_3^+ , CBr_3^+ , and CI_3^+ . All halogens stabilize CX_3^+ relative to CH_3^+ , while the thermodynamic effect of the halogens upon the heavier homologues AX_3^+ ($\text{A} = \text{Si, Ge, Sn, Pb}$) depends on the nature of X. Fluorine has a destabilizing effect upon the heavy-atom cations AF_3^+ ($\text{A} = \text{Si, Ge, Sn, Pb}$). The destabilizing effect decreases and becomes eventually stabilizing for SiX_3^+ , GeX_3^+ , and SnX_3^+ from $\text{X} = \text{fluorine to chlorine, bromine, and iodine}$. The better stabilization of the AX_3^+ cations by heavier halogens is also given by the calculated bond energies of $\text{X}_3\text{A}^+-\text{OH}_2$, which decrease from $\text{F} > \text{Cl} > \text{Br} > \text{I}$. The theoretical data show unequivocally that the thermodynamic stabilization of the AX_3^+ cations ($\text{A} = \text{C, Si, Ge, Sn, Pb}$) by the halogens has the trend $\text{F} < \text{Cl} < \text{Br} < \text{I}$.

The monosubstituted cations AH_2X^+ show that the effect of multiple substitution is not additive, and that the $p(\pi)$ donation alone is not necessarily a measure of thermodynamic stabilization. Calculated isodesmic reaction energies give nearly the same stabilization energy for CH_2F^+ and CH_2Cl^+ , although the chloromethyl cation has a much higher $p(\pi)$ population at carbon. There is only a moderate change in the stabilization of AH_2X^+ by halogen, which has a general trend of increasing stabilization from fluorine to iodine.

The halogens increase the hydride affinity of the neutral compounds YX_3 ($\text{Y} = \text{B, Al, Ga, In, Tl}$) relative to YH_3 . The hydride affinity increases strongly from BF_3 to BI_3 , although the $p(\pi)$ population is much higher in BI_3 than in BF_3 . The bond energies of the complexes $\text{X}_3\text{B}-\text{OH}_2$ are very similar for $\text{X} = \text{fluorine to iodine}$, however. The different affinities of BX_3 for H^- and H_2O demonstrate that the electronic structure of the Lewis acid alone is not sufficient to determine a priori the affinity toward a nucleophilic agent. The bond energy $\text{X}_3\text{B}-\text{L}$ ($\text{L} = \text{Lewis base}$) depends strongly on the nature of the Lewis base. The heavy-atom homologues YX_3 ($\text{Y} = \text{Al, Ga, In, Tl}$) have isodesmic reaction energies and $\text{X}_3\text{Y}-\text{OH}_2$ bond energies which differ less from $\text{X} = \text{F to I}$ than for the boron compounds. The hydride affinities of YH_2X show the same trend but are clearly lower than those of YX_3 .

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Swiss National Science Foundation. We acknowledge excellent service and generous allotment of computer time from the HRZ Marburg, HHLR Darmstadt, and the HLRZ Jülich.

Supporting Information Available: Tables of valence basis sets used in this work, calculated total energies, and optimized bond angles (9 pages). See any current masthead page for ordering and Internet access instructions.

JA970335P