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Publication Date

1976-03-01

Submitted to Journal of the American
Chemical Society

LBL-4934
Preprint c.1

THE PREDICTION OF CORE ELECTRON BINDING ENERGIES WITH A FOUR-PARAMETER EQUATION

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March 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

The Prediction of Core Electron Binding Energies with a Four-Parameter Equation.

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Abstract: Chemical shifts in core electron binding energies can be predicted by the equation $\Delta E_B = \underline{a}F + \underline{b}R$, where the parameters $\underline{a}$ and $\underline{b}$ are characteristic of the class of molecule and atom to which the binding energies pertain, and the parameters F and R are characteristic of substituent groups. The F and R parameters are analogous to the Swain and Lupton $\mathcal{F}$ and $\mathcal{R}$ parameters; i.e., they measure the σ and π electronegativities, respectively, of substituents. However, the F and R values are appropriate only for processes in which a localized positive charge develops on an atom, whereas the $\mathcal{F}$ and $\mathcal{R}$ values are appropriate for ordinary chemical reactions (including both electrophilic and nucleophilic substitutions). Thus lone-pair ionization potentials and proton affinities can be correlated with F and R values more satisfactorily than with $\mathcal{F}$ and $\mathcal{R}$ values.

Introduction

Chemical shifts in core electron binding energies can be equated to the energies of chemical reactions involving ground-state species.[1] For example, the difference between the carbon 1s binding energies of gaseous methane and gaseous carbon dioxide is practically the same as the energy of the following reaction.[2]

$$CH_4 + NO_2^+ \longrightarrow NH_4^+ + CO_2$$

It has been found that, for oxygen-containing compounds (alcohols, ketones, esters, acids, etc.) and amines, shifts in the oxygen 1s and nitrogen 1s binding energies are essentially equal to the negative values of the corresponding shifts in proton affinities.[3-5] It has also been observed[6] that there is a linear correlation between the $-pK_a$ values for acids RCH_2COOH and the iodine $3d_{5/2}$ binding energies of the corresponding iodides RI.

The fact that there is a close correspondence between binding energy shifts and the energies of chemical processes suggests that it should be possible to predict binding energy shifts using the same sorts of correlations and empirical parameters that are used to predict the energies of chemical processes. Indeed, it has recently been shown[7] that the carbon 1s shifts of some substituted benzenes are linearly correlated with the Hammett σ parameters of the substituents. However there are limitations in the use of Hammett parameters, even in the correlation of ordinary chemical data. A given set of σ values can be used to correlate data only for similar chemical systems. To obtain a set of substituent parameters applicable to a wide variety of systems, Swain and Lupton[8] proposed that the Hammett $\sigma\rho$ function be replaced by the sum $\rho f\mathcal{F} + \rho r\mathcal{R}$, in which the parameters ρ, f, and r are characteristic of the substrates and reactions and the parameters $\mathcal{F}$ and $\mathcal{R}$ measure the "field" and "resonance" capabilities of the substituents. For a given set of reactions, ρ is constant and the function $\rho f\mathcal{F} + \rho r\mathcal{R}$ contains effectively only four parameters. Analogous four-parameter functions have been used by other investigators to correlate chemical data. For example, Edwards[9] showed that equilibrium constants of Lewis acid-base reactions can be reproduced by the equation

$$\log(K/K_o) = \alpha E_n + \beta H$$

where K is the equilibrium constant for the reaction of a base with a particular acid and K_o is the constant for the corresponding reaction of a reference base. The parameters α and β are empirical constants characteristic of the acid, and E_n and H are independent parameters for the base. Similarly, Drago and Wayland[10] used a four-parameter equation to correlate <u>heats</u> of dissociation of Lewis acid-base adducts:

$$\Delta H = E_A E_B + C_A C_B$$

The parameters E_A and C_A were assigned to the acids, and the parameters E_B and C_B were assigned to the bases.

In this research we show that it is possible to correlate core electron binding energy shifts by means of the relation

$$\Delta E_B = \underline{a}F + \underline{b}R \qquad (1)$$

in which the parameters <u>a</u> and <u>b</u> are characteristic of the class of molecule and atom to which the binding energies pertain, and the parameters F and R are characteristic of substituent groups. The ΔE_B values are expressed in electron volts, relative to the binding energy of the molecule with a hydrogen atom as the substituent. Thus there are particular values of <u>a</u> and <u>b</u> which correspond to the carbon 1s binding energies of compounds of the type CH_3X, relative to methane. As an example, it is possible to predict the C 1s binding energy of methyl chloride relative to that of methane by substituting these values of a and b and the F and R values for the chloro group into equation 1.

Results and Discussion

We have considered sixteen types of binding energy shifts. Five of these are carbon 1s shifts (for molecules of the type CH_3X, CF_3X, OCX_2, CX_4, and CH_2CHX),[11] two are fluorine 1s shifts (for molecules of the type FX and F_3CX), and the remaining nine are core shifts for boron, silicon, germanium, tin, phosphorus, oxygen, chlorine, bromine, and iodine in molecules containing these elements. We have used data for the following ten substituents (in addition to hydrogen, the reference substituent): CH_3, CF_3, C_6H_5, SiH_3, GeH_3, OCH_3, F, Cl, Br, and I. The sixteen types of binding energy shifts and ten substituents correspond to a total of 160 possible ΔE_B values. Only 92 of these values have been experimentally determined; they were used to evaluate the various a, b, F, and R values. In order to obtain a unique set of these parameters, four of them (the F and R values for CH_3 and the a and b values for CX_4) were arbitrarily fixed. Thus we obtained 92 equations with 48 parameters to be determined. The values of the parameters, determined by a least-squares computer program,[12] are given in Table I and II. The standard errors of the F values are between 0.032 and 0.045; those of the R values are given in Table I. The standard errors of the a values are between 0.37 and 0.50; the standard errors of the b values are between 0.046 and 0.049. The

Table I.

Values of F and R

Substituent	F	R	Std. error of R
CH_3	(0.000)	(- 2.00)	----
CF_3	0.486	- 3.07	0.41
C_6H_5	-0.286	- 0.01	.40
SiH_3	-0.230	- 0.02	.39
GeH_3	-0.258	- 0.70	.41
OCH_3	0.722	- 7.61	.48
F	1.787	-13.88	.99
Cl	0.959	- 7.68	.57
Br	0.624	- 4.53	.44
I	0.451	- 4.28	.39

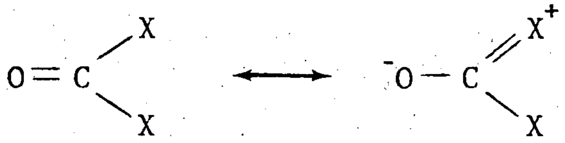
Table II.

Values of <u>a</u> and <u>b</u>

Class of Molecule	a	b	b/a
BX_3	7.21	0.525	0.073
CH_3X	1.97	0.037	.019
$\overset{*}{C}F_3X$	3.76	0.323	.086
$O\overset{*}{C}X_2$	4.58	0.221	.048
CX_4	(8.00)	(0.250)	.031
$\overset{*}{C}H_2CHX$	4.11	0.492	.120
SiX_4	8.22	0.698	.085
GeX_4	7.34	0.600	.082
SnX_4	7.62	0.651	.085
PX_3	7.21	0.576	.080
$\overset{*}{O}CX_2$	8.27	0.985	.119
FX	6.85	0.726	.106
$C\overset{*}{F}_3X$	2.67	0.280	.105
ClX	5.07	0.565	.111
BrX	3.76	0.576	.153
IX	3.46	0.402	.116

experimental and calculated values of the 92 binding energies are listed in Table III. The Gauss criterion for closeness of fit was used; that is, the parameters were chosen to minimize the sum of the squares of the deviations between experimental and calculated values.

The values of the four fixed parameters were chosen so that (1) the trend in F values qualitatively resembles that for electronegativity or σ electron withdrawing power (e.g., the F value for the fluorine atom is greater than that for the methyl group), (2) the trend in R values qualitatively resembles that for π electron withdrawing power (e.g. the R value for a good π donor such as the fluorine atom is more negative than that for a relatively poor π donor such as the methyl group), and (3) all the a and b values are positive. The last restriction is reasonable if one wishes to interpret the a and b values as absolute measures of the sensitivity of the core-ionizing atoms to, respectively, σ and π interactions with substituent groups. The ratio b/a, given in Table II, may be taken as a measure of the π electron sensitivity, relative to the σ electron sensitivity, of the core-ionizing atoms. High values of b/a were found for atoms which can accept negative formal charge from substituents, as in the case of the oxygen atoms of ketones and the β carbon atoms of vinyl compounds.



$$CH_2{=}CH{-}X \longleftrightarrow {}^{-}CH_2{-}CH{=}X^{+}$$

Core ionization of such atoms probably involves a relatively large amount of electronic relaxation in which electron density is shifted to the

Table III.

Experimental and Calculated Binding Energy Shifts

Core Level	Compound	ΔE_B, eV		Ref
		Exptl	Calcd	
B 1s	$B(CH_3)_3$	-0.7	-1.05	29
	$B(OCH_3)_3$	1.0	1.20	29,30
	BF_3	5.7	5.59	29,30
	BCl_3	3.1	2.88	29,30
	BBr_3	1.9	2.12	30
	BI_3	0.7	1.00	30
C 1s	CH_3CH_3	-0.14	-0.07	31
	$\overset{*}{C}H_3CF_3$	1.11	0.84	a
	$\overset{*}{C}H_3C_6H_5$	-0.57	-0.57	b
	CH_3SiH_3	-0.40	-0.46	31
	CH_3GeH_3	-0.52	-0.54	31
	CH_3OCH_3	1.41	1.14	31
	CH_3F	2.8	3.01	32
	CH_3Cl	1.60	1.61	31
	CH_3Br	1.23	1.06	31
	CH_3I	0.6	0.73	6
	$\overset{*}{C}F_3CH_3$	-0.60	-0.65	a
	CF_3CF_3	0.61	0.84	a
	$\overset{*}{C}F_3C_6H_5$	-1.00	-1.08	c
	CF_4	2.72	2.24	a
	CF_3Cl	1.07	1.13	d
	CF_3Br	0.19	0.89	b
	CF_3I	-0.24	0.31	6
	$O\overset{*}{C}(CH_3)_2$	-0.50	-0.44	13
	$O\overset{*}{C}(CF_3)_2$	1.40	1.54	13
	$O\overset{*}{C}(C_6H_5)_2$	-1.3	-1.31	13
	$O\overset{*}{C}(OCH_3)_2$	1.74	1.62	13
	OCF_2	5.26	5.11	13
	$OCCl_2$	2.37	2.69	13

(CONTD.)

Table III. (contd.)

	$\overset{*}{C}(CH_3)_4$	-0.40	-0.50	31
	CF_4	11.05	10.83	31
	CCl_4	5.51	5.75	31
	CBr_4	3.93	3.86	31
	$\overset{*}{C}H_2CHCF_3$	0.8	0.49	a
	$\overset{*}{C}H_2CHOCH_3$	-0.7	-0.78	b
	$\overset{*}{C}H_2CHF$	0.3	0.52	a
	$\overset{*}{C}H_2CHCl$	0.11	0.16	e
	$\overset{*}{C}H_2CHI$	0.2	-0.25	b
Si 2p	$Si(CH_3)_4$	-1.32	-1.40	31
	SiF_4	4.51	5.00	31
	$SiCl_4$	3.11	2.52	31
	$SiBr_4$	2.45	1.97	31
Ge $3p_{3/2}$	$Ge(CH_3)_4$	-1.29	-1.20	31
	GeF_4	4.42	4.78	31
	$GeCl_4$	2.79	2.43	31
	$GeBr_4$	2.02	1.86	31
	GeI_4	1.12	0.74	b
Sn $3d_{5/2}$	$Sn(CH_3)_4$	-1.36	-1.30	35
	$SnCl_4$	2.18	2.31	35
	$SnBr_4$	1.72	1.81	35
	SnI_4	1.01	0.65	35
P $2p_{3/2}$	$P(CH_3)_3$	-1.11	-1.15	36
	PF_3	4.76	4.90	b
	PCl_3	2.73	2.49	36
O 1s	$OC(CH_3)_2$	-1.52	-1.97	13
	$OC(CF_3)_2$	1.08	0.99	13
	$OC(C_6H_5)_2$	-2.63	-2.38	13
	$\overset{*}{O}C(OCH_3)_2$	-1.55	-1.53	13
	OCF_2	1.17	1.11	13
	$OCCl_2$	0.12	0.36	13

(CONTD.)

Table III. (contd.)

F 1s	FCH_3	-1.3	-1.45	32
	FCF_3	1.30	1.10	d
	FC_6H_5	-1.9	-1.97	f
	F_2	2.48	2.17	g
	FCl	0.32	1.00	g
	CF_3CH_3	-0.5	-0.56	a
	CF_3CF_3	0.7	0.44	a
	$CF_3C_6H_5$	-0.7	-0.77	c
	CF_4	0.9	0.88	32
	CF_3Cl	0.4	0.41	d
	CF_3Br	0.15	0.40	b
	CF_3I	0.0	0.00	6
Cl $2p_{3/2}$	$ClCH_3$	-1.15	-1.13	31
	$ClCF_3$	0.52	0.73	d
	ClC_6H_5	-1.28	-1.46	b
	$ClSiH_3$	-1.17	-1.18	31
	$ClGeH_3$	-1.72	-1.70	31
	ClF	1.44	1.22	b,g
	Cl_2	0.42	0.52	31
	ClI	-0.5	-0.14	33
Br $3d_{5/2}$	$BrCH_3$	-0.98	-1.15	31
	$BrCF_3$	-0.23	0.06	b
	BrC_6H_5	-1.03	-1.08	b
	$BrSiH_3$	-0.93	-0.88	31
	$BrGeH_3$	-1.41	-1.37	31
	Br_2	0.04	-0.26	31
	BrI	-1.06	-0.77	33
I $3d_{5/2}$	ICH_3	-0.90	-0.80	14
	ICF_3	0.20	0.45	14
	ICl	0.6	0.23	33
	IBr	-0.07	0.34	33
	I_2	-0.17	-0.16	6

(CONTD.)

Table III. (contd.)

[a]D. W. Davis, Ph.D. Thesis, University of California, Berkeley, Calif., 1973. (Lawrence Berkeley Laboratory Report LBL-1900.) [b]This work. See Experimental Section. [c]S. A. Holmes and T. D. Thomas, J. Am. Chem. Soc., 97, 2337 (1975). [d]S. A. Holmes and T. D. Thomas, unpublished work. [e]A. Berndtsson, E. Basilier, U. Gelius, J. Hedman, M. Klasson, R. Nilsson, C. Nordling, and S. Svensson, Phys. Scr., 12, 235 (1975). [f]D. W. Davis, D. A. Shirley, and T. D. Thomas, J. Am. Chem. Soc., 94, 6565 (1972). [g]T. X. Carroll and T. D. Thomas, J. Chem. Phys., 60, 2186 (1974).

core-ionizing atom from the substituents.[13] The average deviation between the experimental and calculated binding energies in Table III is ±0.20 eV; the standard deviation (calculated on the basis that all the a, b, F, and R parameters are variables) is ±0.37 eV. These deviations are quite reasonable in view of the fact that many of the experimental ΔE_B values are uncertain by as much as ±0.3 eV. (ΔE_B values measured in a given laboratory can have uncertainties of ±0.1 eV or less, but those calculated from absolute values determined in different laboratories are much more uncertain.) Obviously equation 1 can be very useful for prediting unknown core binding energies. As a bonus, the F and R values in Table I give us information regarding the electronegativities and π donor/acceptor abilities of the substituents.

The F and R values are also useful for correlating the energies of any general process in which a positive charge forms on an atom. One process of this type is the ionization of a lone-pair electron, such as a nonbonding valence electron of a halogen atom in a molecular halide. Hashmall et al.[14] have shown that the iodine $3d_{5/2}$ (core) and iodine $5p_{1/2}$ (lone pair) ionization potentials of a series of alkyl iodides are linearly correlated. However, they noticed that the values for hydrogen iodide do not fit the correlation. The corresponding ionization potentials for various other iodides are also not linearly correlated. The lack of general correlation may be explained by the fact that the core ionizations and lone pair ionizations have different relative sensitivities to the π and σ bonding characteristics of the substituents, and hence they have different values for the ratio b/a. Therefore data for various substituents (with essentially independent values for F and R) cannot be linearly correlated. The values for the alkyl iodides are linearly correlated probably because the alkyl groups have very similar R/F values. We have shown that literature values[15-21] of the valence shell lone-pair ionization potentials of various chlorides and iodides can be correlated using equation 1 and the F and R values from Table 1. The least-squares evaluated parameters are, in the case of the 3p ionization potentials of chlorides, a = 4.59 and b = 0.57, and for the $5p_{1/2}$ ionization potentials of iodides, a = 2.50 and b = 0.36. Values of the experimental and calculated binding energies, relative to the values for the hydrogen halides, are given in Table IV. The standard deviations are 0.25 and 0.27 eV, and the average absolute deviations are 0.19 and 0.18 eV, respectively.

Another general process for which energies can be correlated with the F and R values is the addition of a proton to a lone pair of electrons. Several authors have shown that the proton affinities of limited sets of compounds are linearly correlated with the core binding energies of the protonated atoms.[3-5] Again deviations from the linear correlation appear in the case of molecules with markedly different substituents.[5] However we have successfully correlated the proton affinities (PA) of amines, XNH_2, covering the extreme variety of substituents of Table I, using the relation

$$-\Delta(\mathrm{PA}) = \underline{a}F + \underline{b}R$$

In this case the least-squares evaluated parameters a and b are 1.07 and 0.07, respectively. The experimental[22,23] and calculated proton affinities, relative to that for ammonia, are given in Table V. The standard and average absolute deviations are 0.22 and 0.15 eV, respectively.

The F and R values in Table I resemble in some respects the corresponding $\mathcal{F}$ and $\mathcal{R}$ values of Swain and Lupton. However, the sets are fundamentally different (they cannot even approximately be transformed into one another) for two reasons. First, the F and R values apply only to gaseous species and thus are independent of solvent effects that undoubtedly affect the $\mathcal{F}$ and $\mathcal{R}$ values. Second, the F and R values are strictly applicable only to processes in which a localized positive charge develops. The F and R values are therefore principally

Table IV.

Halogen Lone Pair Ionization Potentials

Molecule	IP, eV[a]	Δ(IP), eV		Ref
		exptl	calcd	
CH_3Cl	11.33	-1.46	-1.15	15
CF_3Cl	13.10	0.31	0.47	15
C_6H_5Cl	11.51[b]	-1.28	-1.32	16
SiH_3Cl	11.61	-1.18	-1.07	17
GeH_3Cl	11.30	-1.49	-1.59	17
FCl	12.86	0.07	0.23	18
Cl_2	12.96[c]	0.17	-0.01	19
ICl	12.83	0.04	-0.39	19
HCl	12.79			20
CH_3I	9.85	-0.87	-0.73	21
CF_3I	11.09	0.37	0.10	21
C_6H_5I	10.06[b]	-0.66	-0.72	21
SiH_3I	10.06	-0.66	-0.58	17
GeH_3I	9.86	-0.86	-0.90	17
ClI	10.41	-0.31	-0.39	19
BrI	10.12	-0.60	-0.09	19
I_2	10.56[c]	-0.16	-0.43	19
HI	10.72			20

[a] Vertical IP's. When spin-orbit splitting was observed, average values are used. 3p ionization potentials are reported for the chlorides, and 5p ionization potentials for the iodides. [b] The average of the symmetry-split bands. [c] The average of the $^2\Pi_g$ and $^2\Pi_u$ states.

Table V.

Proton Affinities of XNH_2 Molecules

Molecule	PA, kcal/mol	$-\Delta(PA)$, eV		Ref
		exptl	calcd	
CH_3NH_2	211	-0.39	-0.14	23
CF_3NH_2	196	0.26	0.30	a
$C_6H_5NH_2$	209	-0.30	-0.31	23
SiH_3NH_2	204	-0.09	-0.25	a
GeH_3NH_2	207	-0.22	-0.33	a
CH_3ONH_2	201	0.04	0.24	a
FNH_2	182	0.87	0.94	a
$ClNH_2$	190	0.52	0.49	a
$BrNH_2$	189	0.57	0.35	a
INH_2	188	0.61	0.18	a
NH_3	202			23

[a] See Calculations Section

affected by the <u>donor</u> abilities of the substituents and are relatively independent of the <u>acceptor</u> abilities. (A good donor is not necessarily a poor acceptor, and vice versa.) On the other hand, the $\mathcal{F}$ and $\mathcal{R}$ values were set up to be applicable to a wide variety of processes, including both nucleophilic and electrophilic reactions. Hence the $\mathcal{F}$ and $\mathcal{R}$ values reflect both donor and acceptor characteristics. Probably these facts can be used to explain the fact that the R value for the CF_3 group is negative, whereas the corresponding $\mathcal{R}$ value is positive. In a core ionization, the π acceptor ability of a substituent is relatively unimportant compared to its π donor ability. Hence the low negative R value for CF_3, indicating that CF_3 is a fairly poor π donor, is reasonable. However in many other chemical processes, the strong π acceptor ability of CF_3 is important. The positive $\mathcal{R}$ value reflects this ability. Obviously $\mathcal{F}$ and $\mathcal{R}$ values represent a compromise in the measure of donor and acceptor properties. It is significant that the lone pair ionization potential data and proton affinity data of Tables IV and V are very poorly correlated if $\mathcal{F}$ and $\mathcal{R}$ values are used instead of F and R values.[24]

<u>Calculations</u>

<u>Core Binding Energies</u>. - The B 1s chemical shift between BH_3 and BF_3 was calculated on the basis of the equivalent cores approximation[1] from the heat of the following reaction.

$$BH_3 + CF_3^+ \longrightarrow BF_3 + CH_3^+$$

The heat of formation of BH_3 (20.5 kcal/mol) was calculated from the data of Garabedian and Benson[25] and Gunn and Green.[26] The heat of formation of CF_3^+ (99.3 kcal/mol) was taken from McMahon <u>et al.</u>,[27] and the heats of formation of BF_3 and CH_3^+ were taken from the tables of Franklin et al.[28] These data lead to $\Delta E_B = -5.7$ eV. The ΔE_B values for the other boron compounds[29,30] (relative to BF_3) were added to 5.7 eV to obtain the values in Table III. The C 1s binding energy of CH_4 (290.71 eV) is derived from measurements of Perry and Jolly.[31] The C 1s binding energies of CHF_3,[32] H_2CO,[33] and C_2H_4[34] are 8.30, 3.50, and -0.1 eV, respectively, relative to CH_4. The core binding energies of SiH_4 and GeH_4 were taken from Perry and Jolly;[31] that of SnH_4 from Avanzino and Jolly,[35] and that of PH_3 from Perry, Schaaf and Jolly.[36] The O 1s binding energy of H_2CO has been determined[37] to be -3.77 eV, relative to the main peak of O_2 (for which we have measured $E_B = 543.21$ eV). From these data we calculate E_B = 539.44 eV, in good agreement with the value 539.42 eV reported by Carroll, Smith and Thomas.[5] The F 1s binding energies of HF and CHF_3 have been reported as 694.22 eV[38] and -0.9 eV (relative to CF_4)[32], respectively. The core binding energies of HCl and HBr were taken from Perry and Jolly.[31] The I $3d_{5/2}$ binding energy of HI is -0.20 eV[14] (relative to CF_3I) and that of CF_3I is 627.76 eV.[6] The latter compound was used as a reference for most of the other $\overset{*}{C}F_3X$ compounds.

Proton Affinities. - In the case of each of the amines except CH_3NH_2, $C_6H_5NH_2$, and NH_3, we calculated the proton affinity from the sum of the energies of reactions 2 and 3, in which all species are gaseous. We

$$XNH_3^+ + CH_4 \longrightarrow XCH_3 + NH_4^+ \qquad (2)$$

$$\underline{XCH_3 + NH_4^+ \longrightarrow XNH_2 + H^+ + CH_4} \qquad (3)$$

$$XNH_3^+ \quad XNH_2 + H^+$$

used the equivalent cores approximation[1]; that is, we assumed that the energy of reaction 2 is equal to the difference between the C 1s binding energy of CH_4 and that of XCH_3. The appropriate $-\Delta E_B$ values were taken from Table III. When available, the heats of formation of species in reaction 3 were taken from the literature.[28,39,40] In some cases the heats of formation were estimated, as follows. The heat of formation of SiH_3CH_3 was assumed to be the average of the heats of formation of Si_2H_6 and C_2H_6 minus the quantity $23(\Delta x)^2$ kcal/mol, where Δx is the difference in the Pauling electronegativities of silicon and carbon.[41] (Calcd $\Delta H_f^\circ = -12$ kcal/mol.) A similar procedure was used to calculate the heats of formation of GeH_3CH_3 (-2), CF_3NH_2 (-149), SiH_3NH_2 (-12), GeH_3NH_2 (-2), $BrNH_2$ (14), and INH_2 (13). The heats of formation calculated by this method for FNH_2 and $ClNH_2$ are very close to those calculated from the formula $\Delta H_f^\circ = \frac{1}{3}\Delta H_f^\circ(NX_3) + \frac{2}{3}\Delta H_f^\circ(NH_3)$. We used $\Delta H_f^\circ(FNH_2) = -16$ and $\Delta H_f^\circ(ClNH_2) = 12$. The heat of formation of a methoxy compound is generally about 7 kcal/mol higher than that of the corresponding hydroxy compound. Hence we added 7 to $\Delta H_f^\circ(NH_2OH)$[40] to obtain $\Delta H_f^\circ(CH_3ONH_2) = -6$.

Experimental

Spectra were obtained with the Berkeley iron-free, double-focusing magnetic spectrometer.[42] Magnesium K_α x-rays were used as the photoionizing radiation, except in the case of GeI_4, for which aluminum K_α x-rays were used. The spectra of $C_6H_5CH_3$, C_6H_5Cl, CH_2CHI, PF_3 and ClF were referenced against the Ar $2p_{3/2}$ line (248.45 eV), and the spectra of CF_3Br, CH_2CHOCH_3, GeI_4 and C_6H_5Br against the Ne 1s line (870.23 eV). Binding energies were determined by a least-squares fit of the experimental data to Lorentzian lineshapes. Our measured binding energies are believed to be accurate to ±0.05 eV, except for GeI_4 (±0.1 eV).

Reagent grade toluene and chlorobenzene were used without further purification. Bromobenzene was purified by distillation, bromotrifluoromethane was obtained from PCR, Inc., methyl vinyl ether from the Matheson Co., Inc., phosphorus trifluoride from Research Organic/Inorganic Chemical Corp., and chlorine monofluoride from Ozark-Mahoning, Inc. Vinyl iodide was prepared by the method of Spence,[43] and its purity checked by nmr.[44] Germanium tetraiodide was prepared by the method of Foster and Williston[45] and was purified by vacuum sublimation.

Acknowledgments

This research was supported by the National Science Foundation (Grant CHE73-05133 A02) and The Energy Research and Development Administration. We are grateful to Michael McKelvy for preparing the vinyl iodide and to Steven Avanzino, Theodore Schaaf, and Winfield Perry for assistance with the XPS measurements.

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