J. Org. Chem. **1989**, *54*, 5132–5137

Correlation of Thermochemical Data with Gas-Phase Ionization Potentials

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Received December 8, 1988

Enthalpies of formation of mono- to tetrahalomethanes are linearly related to the respective sums of the ionization potentials of the halogen(s) and the hydrogen(s) in the molecule. Similar correlations seem to hold for enthalpies of formation of halogenated ethanes, ethenes, and benzenes. Analogous correlations between enthalpies of formation of CH_3COX (X = F, Cl, Br, and I), MeHgX (X = Cl, Br, and I), Me_3SiX (X = F, Cl, and Br), *n*-Bu_2BX (X = Cl, Br, and I), and the ionization potential of X are also reported. Enthalpies of formation of Et_2Y and $F_2C{=}Y$ (Y = O, S, and Se) plot linearly against the first gas-phase ionization potential of the heteroatom. Thermochemical data of the triphenyl derivatives Ph_3E (E = N, P, As, Sb, and Bi) seem to exhibit a linearity with respect to the first gas-phase ionization potential of the central atom. Enthalpies of formation of compounds of the general structure $R^1R^2R^3CX$, where R^i = H, Me, or Et, are shown to correlate with the respective sums of the ionization potentials of the free radicals that correspond to R^i plus the ionization potential of X. The latter may be a halogen atom or a group such as OH, SH, NH_2, etc. When X involves elements of the same group, the plots appear as cross correlations. The implications of the cross correlations are discussed. Enthalpies of formation of halogenated methyl radicals also exhibit the above-mentioned linear dependence on the respective sums of the IP(X,H)'s, leading to a cross correlation. Enthalpies of formation of alkyl free radicals of the general structure $R^1R^2R^3C^\bullet$, R^i = H, Me, or Et, plot linearly against the respective sums of the ionization potentials of the free radicals that correspond to R^i. All these correlations may imply that the contribution of the halogen, hydrogen methyl, and ethyl groups to the enthalpy of formation is transferable and/or additive. It is concluded that the enthalpies of formation of fluorinated methyl radicals that are perfectly consistent with the recent values for halogenated methyl radicals of Holmes and Lossing are as follows: $CH_2F^\bullet$, −85.5; $CHF_2^\bullet$, −273.0; $CF_3^\bullet$, −460 kJ/mol (all ±10 kJ/mol). It is suggested that the ionization potential of any free radical may function as a substituent constant.

The thermochemical parameters of organic compounds are of great importance for a multitude of reasons. They enable one to calculate enthalpies and the thermodynamic feasibility of reactions. enthalpies of formation also form the basis for calculating the various types of bond dissociation energies. In addition they help us understand matters such as cohesion, boiling points, and spectral properties.[1,2] Homologous series of compounds *n*-R–X, where X = e.g. H, Br, OH, and SH, exhibit a remarkable general property with respect to thermochemistry. Almost any thermochemical parameter, including zero-point energies,[3] of the above-mentioned series plots linearly against the respective number of carbon atoms in the *normal* alkyl chain.[1] Even for compounds R_nE, where E is a metal (e.g., Al) or nonmetal (e.g., N), the linearity between, e.g., enthalpies of formation and the respective sums of carbon numbers, still holds, as can be seen in the example of Figure 1. This can be taken as a manifestation of the fact that the methylene contribution to the thermochemical parameter is transferable as well as additive[4] in an intraseries manner. The correlation in Figure 1 also indicates that the effect of a normal alkyl chain for the thermochemical parameters is strictly additive. Transferability and additivity often hold in an interseries fashion as well. For example, one can obtain the methylene contribution to the enthalpy of vaporization from the series of *n*-RBr and use it for the estimation of the enthalpy of vaporization of *n*-butanethiol by adding it twice to the enthalpy of vaporization of ethanethiol, with an uncertainty comparable to the experimental one.

Contrary to the above-mentioned regularity with which a given thermochemical parameter varies with increasing alkyl chain length, things appear to be more complex if one considers the factors influencing the variation of the thermochemical parameters among isomeric compounds, or analogous compounds, e.g., Ph_3E, where E = N, P, As, Sb, and Bi. Even more serious is the problem when one tries to rationalize the effect of accumulated heteroatoms in an organic molecule with respect to thermochemical parameters of the molecule. For example, if we consider the enthalpies of formation of methyl halides, we notice that the value becomes decreasingly negative as the electronegativity of the halogen decreases. Now, if we consider the effect of increasing numbers of the electronegative atom, e.g., in CH_3F, CH_2F_2, CHF_3, and CF_4, we notice that the enthalpy of formation becomes increasingly negative with increasing number of fluorine atoms. Conventional electronegativities, e.g., Pauling's, are not additive parameters. In fact, according to Sanderson,[5] when atoms of different electronegativity combine to form a compound, they become adjusted to the same intermediate electronegativity within the compound. Therefore, it appears hopeless to try to find a simple relationship between thermochemical data and the electronegativities of the atoms that comprise the molecule. Only for bond dissociation energies has a complex relationship with electronegativity differences been derived by Matcha.[6]

To explain the differences between enthalpies of formation for isomeric hydrocarbons, Pitzer and Catalano[3] invoked dispersion energies arising from interaction between nonbonded C–H groups. Similar interactions could possibly occur in halogenated alkanes. Bearing in mind that carbon–halogen bonds are by far more polirizable than C–H bonds, it should be expected that energies of nonbonded interactions involving C–X bonds would be much greater. Since the expression for dispersion energy involves, inter alia, ionization potentials, it appeared logical to us to attempt to correlate thermochemical data such as enthalpies of formation with gas-phase ionization potentials. From our previous work it was known that ionization potentials of alkyl free radicals and of a hydrogen atom behave as additive parameters.[7] For example, heterolytic[7] as well as homolytic[8] bond dissociation energies have been

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[1] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970; Chapter 6.

[2] Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell Scientific Publications: Oxford, 1985.

[3] Pitzer, K. S.; Catalano, E. *J. Am. Chem. Soc.* **1956**, *78*, 4844.

[4] Bader, R. F. W.; Carroll, M. T.; Cheesman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968, and references therein.

[5] Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112.

[6] Matcha, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4859.

[7] Screttas, C. G. *J. Org. Chem.* **1979**, *44*, 1471.

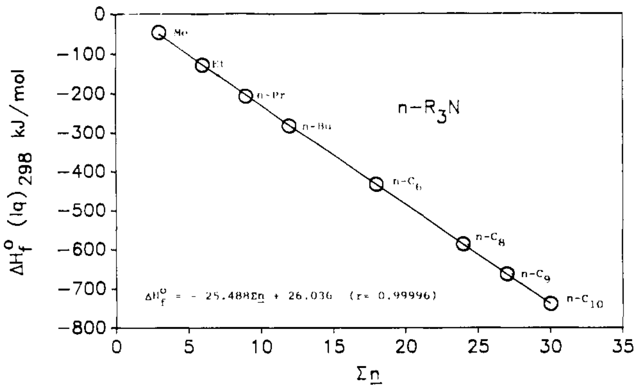

Figure 1. Enthalpies of formation (liquid, 298.15 K in kJ/mol) of tri-*n*-alkylamines plotted against the respective sums of carbon numbers: Me, –45.7; Et, –127.7; *n*-Pr, –207.1; *n*-Bu, –281.6; *n*-C_6, –433.0; *n*-C_8, –585.0; *n*-C_9, –661.5; *n*-C_{10}, –738.0 (data from ref 10).

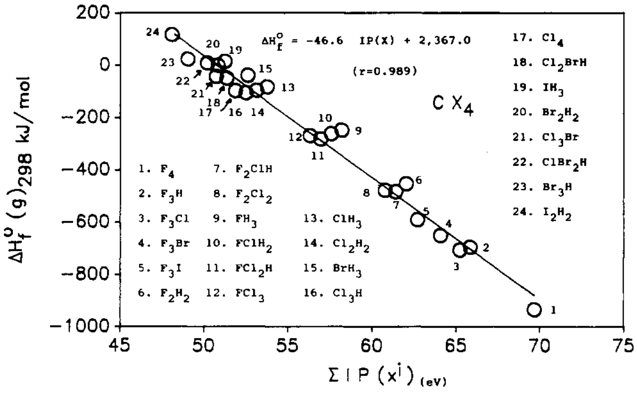

Figure 2. Enthalpies of formation (gas, 298.15 K in kJ/mol) of halomethanes correlated with the respective sums of the ionization potentials of the halogen(s) and hydrogen(s): CF_4, –933.6; CHF_3, –695.0; $CClF_3$, –706.3; $CBrF_3$, –650.0; CIF_3, –590.0; CH_2F_2, –453.0; $CHClF_2$, –483.5; CCl_2F_2, –477.5; CH_3F, –247.0; CH_2FCl, –261.0; $CHFCl_2$, –281.0; $CFCl_3$, –268.0; CH_3Cl, –82.0; CH_2Cl_2, –95.7; CH_3Br, –38.1; $CHCl_3$, –104.8; CCl_4, –97.1; $CHBrCl_2$, –49.0; CH_3I, 15.4; CH_2Br_2, 0.0; $CBrCl_3$, –43.7; $CHBr_2Cl$, 9.0; $CHBr_3$, 23.8; CH_2I_2, 118. IP(X)'s (eV): F, 17.422; Cl, 12.967; Br, 11.814; I, 10.451; H, 13.598 (all data from ref 12).

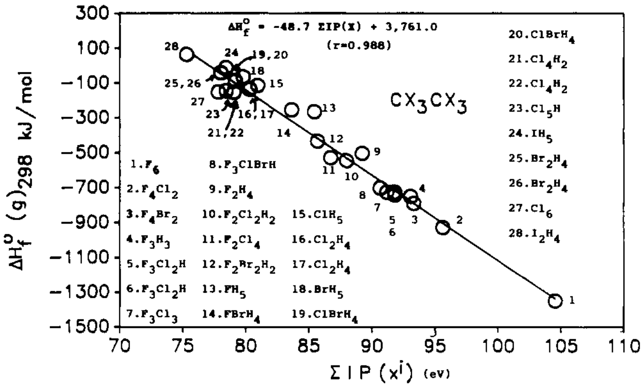

Figure 3. Enthalpies of formation (gas, 298.15 K, kJ/mol) of haloethanes plotted as in Figure 2: CF_3CF_3, –1348.0; $ClCF_2CF_2Cl$, –925.0; $BrCF_2CF_2Br$, –789.0; CH_3CF_3, –749.0; CF_3CHCl_2, –740.0; $CF_2ClCHFCl$, –724.0; CF_3CCl_3, –725.0; $CF_3CHBrCl$, –700.0; CH_3CHF_2, –501.0; CF_2ClCH_2Cl, –543.0; $CFCl_2CFCl_2$, –527.0; CF_2BrCH_2Br, –431.0; CH_3CH_2F, –263.0; CH_2FCH_2Br, –251.0; CH_3CH_2Cl, –112.1; $ClCH_2CH_2Cl$, –134.0; CH_3CHCl_2, –131.0; CH_3CH_2Br, –62.3; $BrCH_2CH_2Cl$, –87.0; $CH_3CHBrCl$, –83.0; $ClCH_2CCl_3$, –152.0; $CHCl_2CHCl_2$, –150; Cl_3CCHCl_2, –143.0; CH_3CH_2I, –9.0; $BrCH_2CH_2Br$, –39.0; CH_3CHBr_2, –37.0; Cl_3CCl_3, –150.0; ICH_2CH_2I, 66.3 (data from ref 12).

shown to be linearly related to ionization potentials of alkyl free radicals.

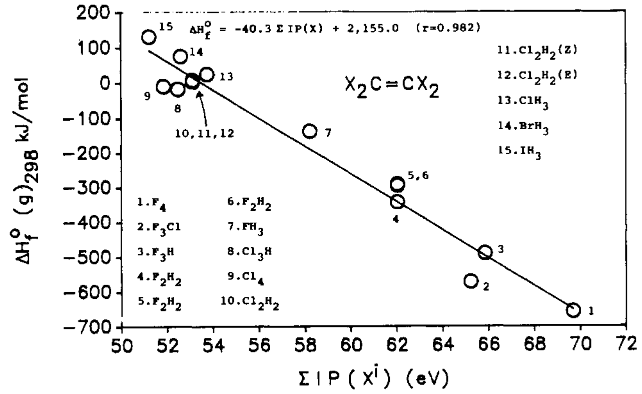

Figure 4. Enthalpies of formation (gas, 298.15 K, kJ/mol) of haloethenes plotted as in Figure 2: $CF_2{=}CF_2$, –659.0; $CFCl{=}CF_2$, –573.0; $CHF{=}CF_2$, –491.0; $CH_2{=}CF_2$, –345.0; *Z*-$FCH{=}CHF$, –297.0; *E*-$FCH{=}CHF$, –293.0; $Cl_2C{=}CCl_2$, –11.0; $CHCl{=}CCl_2$, –19.0; $CH_2{=}CCl_2$, 2.3; *Z*-$CHCl{=}CHCl$, 4.0; *E*-$ClCH{=}CHCl$, 6.0; $CH_2{=}CHF$, –138.8; $CH_2{=}CHCl$, 23.0; $CH_2{=}CHBr$, 73.9; $CH_2{=}CHI$, 130.0 (data from ref 12).

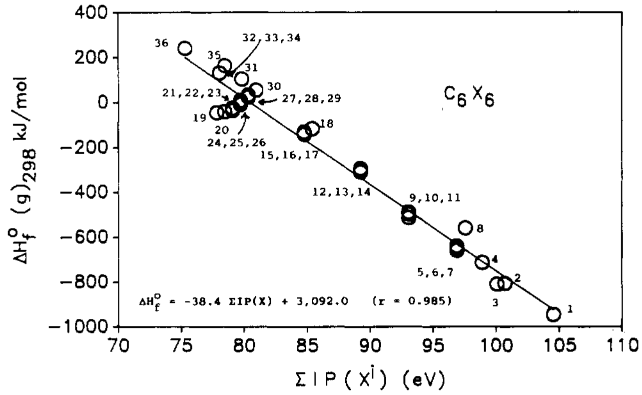

Figure 5. Enthalpies of formation (gas, 298.15 K, kJ/mol) of halobenzenes plotted as in Figure 2: 1, C_6F_6, –946.0; 2, C_6F_5H, –806.0; 3, C_6F_5Cl, –810.0; 4, C_6F_5Br, –712.0; 5, $C_6F_4H_2$ (1, 2, 3, 4), –638.0; 6, $C_6F_4H_2$ (1, 2, 3, 5), –657.0; 7, $C_6F_4H_2$ (1, 2, 4, 5), –647.0; 8, C_6F_5I, –558.0; 9, $C_6F_3H_3$ (1, 3, 5), –512.0; 10, $C_6F_3H_3$ (1, 2, 3), –488.0; 11, $C_6F_3H_3$ (1, 2, 5), –496.0; 12, $C_6F_2H_4$ (1, 2), –293.8; 13, $C_6F_2H_4$ (1, 3), –309.2; 14, $C_6F_2H_4$ (1, 4), –306.6; 15, C_6FClH_4 (1, 4), –141.0; 16, C_6FClH_4 (1, 3), –140.0 17, C_6FClH_4 (1, 2), –130.0; 18, C_6FH_5, –116.0; 19, C_6Cl_6, –44.7; 20, C_6Cl_5H, –40.0; 21, $C_6Cl_4H_2$ (1, 2, 3, 4), –25.4; 22, $C_6Cl_4H_2$ (1, 2, 4, 5), –32.6; 23, $C_6Cl_4H_2$ (1, 2, 3, 5), –34.9; 24, $C_6Cl_3H_3$ (1, 2, 3), –8.1; 25, $C_6Cl_3H_3$ (1, 3, 5), 0.0; 26, $C_6Cl_3H_3$ (1, 2, 4), 8.1; 27, $C_6Cl_2H_4$ (1, 4), 24.6; 28, $C_6Cl_2H_4$ (1, 3), 28.1; 29, $C_6Cl_2H_4$ (1, 2), 33.0; 30, C_6ClH_5, 54.4; 31, C_6BrH_5, 104.3; 32, $C_6Br_2H_4$ (1, 2), 132.0; 33, $C_6Br_2H_4$ (1, 3), 131.0; 34, $C_6Br_2H_4$ (1, 4), 131.0; 35, C_6IH_5, 164.9; 36, $C_6I_2H_4$ (1, 4), 241.0 (data from ref. 12).

Our initial attempt concerned the correlation of enthalpies of formation of tetrahalomethanes with the respective sums of the ionization potentials of the halogens, which turned out to be successful. We noticed that the same correlation could accommodate data of halomethanes with a variable number of halogen atoms, including monohalides (Figure 2). It must be emphasized that in the sum of the ionization potentials the ionization potential of the hydrogen(s) is included as well. A similar correlation is shown in Figure 3, which involves enthalpies of formation of mono- to hexahaloethanes. In Figure 4 are plotted the enthalpies of formation of mono- to tetrahaloethenes, and in Figure 5 the enthalpies of formation of mono- to hexahalobenzenes, against the respective sums of ionization potentials of the halogens and hydrogens. The correlations in Figures 2–5 exhibit a rather marked scatter. For ex-

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(8) Screttas, C. G. *J. Org. Chem.* **1980**, *45*, 1620.

ample, in the case of the CX_4 correlation, Figure 2, some points are as much as 30% off the value calculated from the regression equation. Therefore, these correlations appear to be of rather limited value for predicting enthalpies of formation. However, they may just reflect the great range of the data covered by the correlations. For example, the correlation in Figure 3 involves data with ranges of 1414 kJ/mol (4.184 kJ = 1 kcal) and 29.2 eV (1 eV = 23.05 kcal) in the enthalpies of formation and the sums of the ionization potentials, respectively. It is felt that the scatter observed in these correlations is due to the rather large uncertainty involved in the enthalpies of formation of halogenated organic compounds, which, like other thermochemical data, are under continuous revision. The correlations in Figures 3–5 are not sensitive enough to distinguish between positional or (in case of haloethenes) geometric isomers. Indeed, the correlations predict that compounds of the same category that have equal sums of ionization potentials should have equal enthalpies of formation. This seems to be realized in certain instances. For example, the compounds $ClCH_2CCl_3$ and $Cl_2CHCHCl_2$ have equal sums of IP(X,H)'s, and their enthalpies of formation are −152 and −150 kJ/mol, respectively. This fact then might suggest that the halogen and hydrogen contributions to the enthalpy of formation of halogenated compounds could be transferable and/or additive.[9] If this is so, then one can write the redistribution eq 1,

$$\underset{1}{2CF_2ClCH_2Cl} = \underset{2}{CF_2ClCF_2Cl} + \underset{3}{ClCH_2CH_2Cl} \qquad (1)$$

for example, and hence $\Delta H_f°(\mathbf{1}) = 0.5[\Delta H_f°(\mathbf{2}) + \Delta H_f°(\mathbf{3})] = 0.5[(-925) + (-134)] = -529.5$ kJ/mol. This value is 13.5 kJ/mol less negative than the experimental value, −543 kJ/mol.

Example 2:

$$\underset{4}{2CF_2{=}CHCl} = \underset{5}{CF_2{=}CF_2} + \underset{6}{E\text{-}ClCH{=}CHCl} \qquad (2)$$

and hence $\Delta H_f°(\mathbf{4}) = 0.5[\Delta H_f°(\mathbf{5}) + \Delta H_f°(\mathbf{6})] = 0.5[(-659) + (6)] = -326.5$ kJ/mol, i.e., 10.5 kJ/mol more negative than the experimental value, −316 kJ/mol.

Example 3:

$$\underset{7}{2CBrCl_3} = \underset{8}{CCl_4} + \underset{9}{CBr_2Cl_2} \qquad (3)$$

and hence $\Delta H_f°(\mathbf{7}) = 0.5[\Delta H_f°(\mathbf{8}) + \Delta H_f°(\mathbf{9})] = 0.5[(-97.1) + (8)] = -44.6$ kJ/mol, 1.9 kJ/mol more negative than the experimental value, −42.7 kJ/mol.

One should not expect a better agreement between the predicted value and the experimental one because this simple estimating scheme ignores contributions from nonbonded interactions. There are other more accurate methods for estimating enthalpies of formation.[10]

As a corollary of these correlations, it follows that *sets of thermochemical data in two different correlations that involve the same sets of IP(X)'s or sums of IP(X)'s are linearly related to each other.* This point is demonstrated by the correlation between the enthalpies of formation of CX_4 and $X_2C{=}CX_2$, eq 4 ($\Delta H_f°$'s are in kJ/mol). The

$$\Delta H_f°(X_2C{=}CX_2) = 0.85\Delta H_f°(CX_4) + 84.0 \quad (r = 0.994) \qquad (4)$$

correlation includes the following points: $X_4 = F_4$, F_3Cl, F_3H, F_2H_2, Cl_4, Cl_3H, Cl_2H_2, FH_3, ClH_3, BrH_3, IH_3.

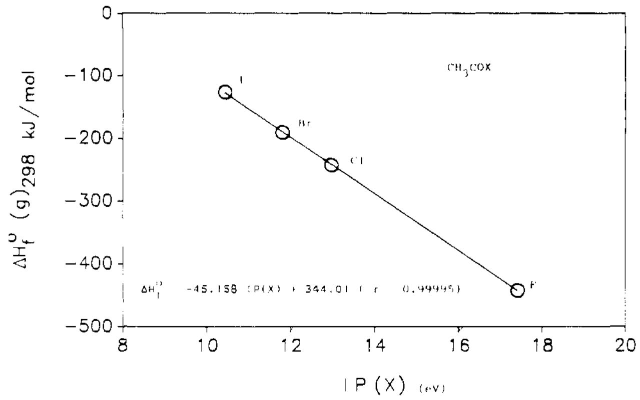

Figure 6. Enthalpies of formation (gas, 298.15 K, kJ/mol) of acetyl halides plotted against the ionization potential of the halogen: CH_3COF, −442.1; CH_3COCl, −242.8; CH_3COBr, −190.4; CH_3COI, −126.4 (data from ref 12).

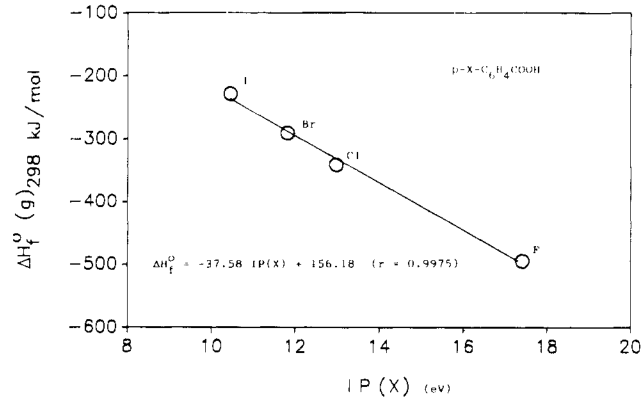

Figure 7. Enthalpies of formation (gas, 298.15 K, kJ/mol) of *p*-halobenzoic acids plotted as in Figure 6: X = F, −494.5; Cl, −341.0; Br, −290.4; I, −228.1 (data from ref 12).

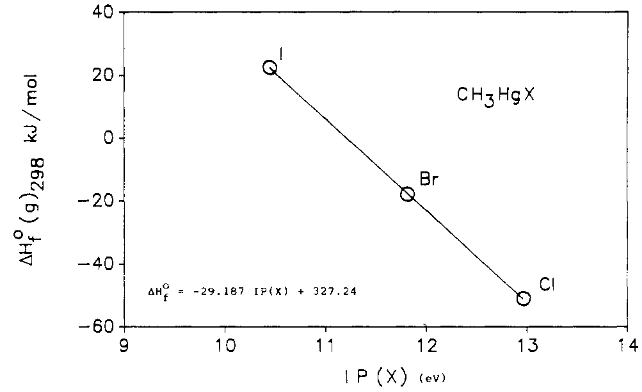

Figure 8. Enthalpies of formation (gas, 298.15 K, kJ/mol) of methylmercury halides plotted as in Figure 6: MeHgCl, −51.0; MeHgBr, −18.0; MeHgI, 22.4 (data from ref 12).

Enthalpies of formation of halogen-bearing carboxylic acid derivatives do correlate with IP(X)'s. For example, the correlation in Figure 6 covers the acetyl halides, and that is Figure 7 the *p*-halobenzoic acids. The correlation in Figure 6 exhibits a perfect correlation coefficient, and this, perhaps, is indicative of the utility of this type of correlation for predicting enthalpies of formation or for checking the internal consistency of the data.

So far we have examined correlations involving halogenated organic compounds. The question then arises as to whether analogous correlations hold in cases where the halogen atom is bonded to elements other than carbon. The answer seems to be positive. For example, enthalpies

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(9) This possibility has been pointed out by Professor Joel F. Liebman, of the University of Meryland, Baltimore, to whom we are deeply indebted.

(10) See, e.g.: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986; Chapter 2.

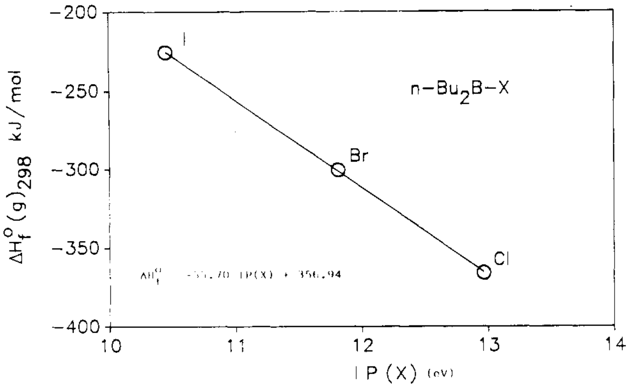

Figure 9. Enthalpies of formation (gas, 298.15 K, kJ/mol) of di-*n*-butylhaloboranes plotted as in Figure 6: *n*-Bu_2BCl, -365.7; *n*-Bu_2BBr, -300.4; *n*-Bu_2BI, -225.5 (data from ref 1, Chapter 5).

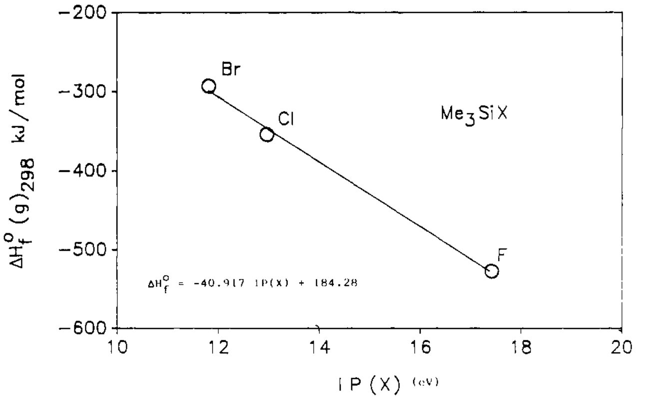

Figure 10. Enthalpies of formation (gas, 298.15 K, kJ/mol) of trimethylhalosilanes plotted as in Figure 6: Me_3SiF, -527.0; Me_3SiCl, -354.0; Me_3SiBr, -293.0 (data from ref 12).

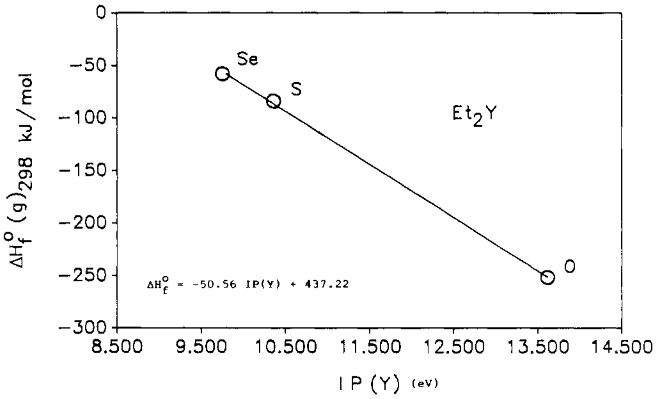

Figure 11. Enthalpies of formation (gas, 298.15 K, kJ/mol) of Et_2O, Et_2S, and Et_2S plotted against the first gas-phase ionization potential of the hetroatom: Et_2O, -251.7; Et_2S, -84.0; Et_2Se, -58.0. IP(Y)'s (eV): Y = O, 13.618; S, 10.360; Se, 9.752 (data from ref 12).

of formation of MeHgX, *n*-Bu_2BX, and Me_3SiX plot linearly against the respective IP(X)'s (Figures 8–10, respectively). From the correlations in Figures 8–9, we obtain by extrapolation the enthalpies of formation of MeHgF and *n*-Bu_2BF, -181 ± 10 and -613 ± 20 kJ/mol, respectively.

The next question to be answered is whether ionization potentials other than those of halogen and hydrogen atoms can be employed in relevant correlations. In Figure 11 are plotted the enthalpies of formation of diethyl ether, diethyl sulfide, and diethyl selenide against the first gas-phase ionization potential of the heteroatom. Figure 12 shows a closely analogous correlation involving data of $F_2C{=}Y$

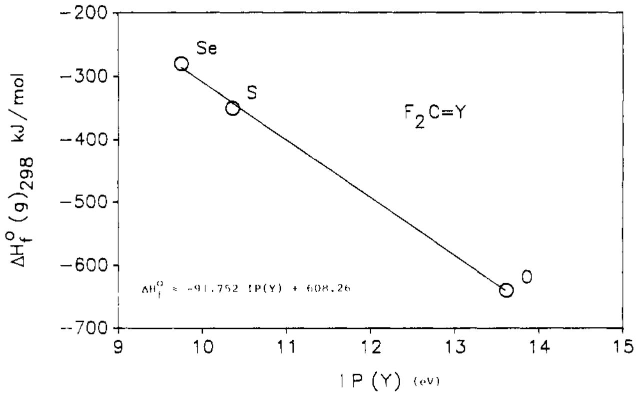

Figure 12. Enthalpies of formation (gas, 298.15 K, kJ/mol) of chalcogenocarbonyl difluorides plotted as in Figure 11: $F_2C{=}O$, -640.0; $F_2C{=}S$, -350.0; $F_2C{=}Se$, -280.

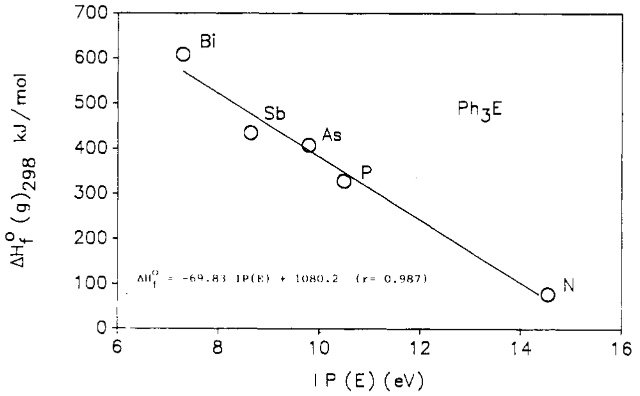

Figure 13. Enthalpies of formation (gas, 298.15 K, kJ/mol) of the triphenyl derivatives of the group 5A elements plotted against the first gas-phase ionization potential of the central atom: Ph_3N, 78.0; Ph_3P, 328.0; Ph_3As, 408.0; Ph_3Sb, 435.0; Ph_3Bi, 609.0. IP's (eV): N, 14.534; P, 10.486; As, 9.788; Sb, 8.641; Bi, 7.289 (data from ref 12).

(Y = O, S, Se). Enthalpies of formation of triphenyl derivatives of N, P, As, Sb, and Bi are correlated with the first gas-phase ionization potential of the central atom (Figure 13). Obviously all three plots do provide a positive answer to the above-stated question. On the basis of the correlation in Figure 11, we predict the enthalpy of formation of Et_2Te to be -18 kJ/mol. Similarly, from the correlation in Figure 12 we estimate the enthalpy of formation of $F_2C{=}Te$ to be -218 kJ/mol.

We found that ionization potentials of more complex molecular entities can be employed in analogous correlations. In this connection we examined data of compounds of the general structure $R^1R^2R^3C{-}X$. Enthalpies of formation of the series CH_3X, EtX, *n*-PrX, *s*-PrX, *s*-BuX, and *t*-BuX, where X = e.g. halogen, OH, SH, NH_2, $CH{=}O$, etc., plot linearly against the respective sums of the ionization potentials of the hydrogen(s) and the free radicals $Me^\bullet$ and $Et^\bullet$. For example, the sum of the ionization potentials of *s*-BuX, (Et)(Me)CHX, is equal to $IP(Et^\bullet) + IP(Me^\bullet) + IP(H^\bullet) = 8.13 + 9.84 + 13.598 = 31.568$ eV. An example of such a correlation is given in Figure 14, for X = $CH{=}O$. An implication of these correlations is that the enthalpies of formation of any two sets of the above-mentioned alkyl derivatives are linearly related to each other, e.g., eq 5.

$$\Delta H_f^\circ(R^1R^2R^3CCH{=}O) = 0.73\Delta H_f^\circ(R^1R^2R^3COH) - 19.6 \quad (r = 0.997) \quad (5)$$

The above correlations may imply transferability and/or additivity of the H, Me, and Et group contributions to the

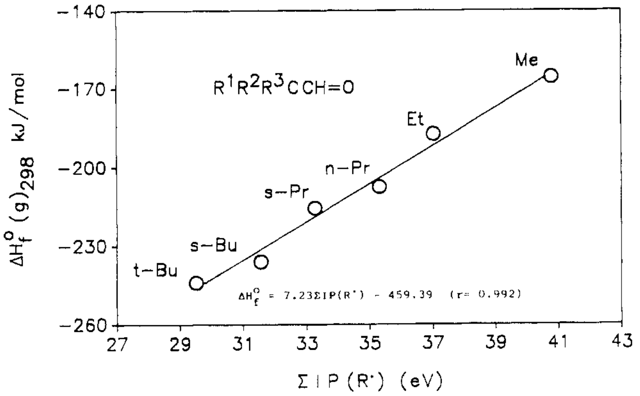

Figure 14. Enthalpies of formation (gas, 298.15 K, kJ/mol) of aldehydes of the general structue $R^1R^2R^3CCH{=}O$, where R^i = H, Me, Et, plotted against the respective sums of the ionization potentials of the free radicals that correspond to R^i: MeCH=O, −165.8; EtCH=O, −187.4; *n*-PrCH=O, −207.5; *s*-PrCH=O, −215.6; *s*-BuCH=O, −236.0; *t*-BuCH=O, −244.0. IP ($R^{i\bullet}$) (eV): $H^\bullet$, 13.598; Me, 9.84; Et, 8.13 (all data from ref 12).

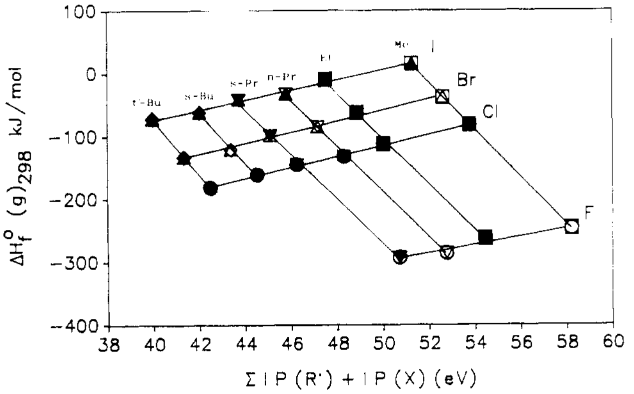

Figure 15. Enthalpies of formation (gas, 298.15 K, kJ/mol) of alkyl halides of the general structure $R^1R^2R^3CX$, R^i = H, Me, or Et, plotted against the sum of the ionization potentials of the free radicals or hydrogen atom that correspond to R^i plus the ionization potential of the halogen. X = F: Me, −247.0; Et, −263.0; *n*-Pr, −286.0; *s*-Pr, −293.0. X = Cl: Me, −82.0; Et, −112.1; *n*-Pr, −132.4; *s*-Pr, −145.0; *s*-Bu, −161.0; *t*-Bu, −182.0. X = Br: Me, −38.1; Et, −62.3; *n*-Pr, −84.5; *s*-Pr, −98.3; *s*-Bu, −120.9; *t*-Bu, −133.0. X = I: Me, 15.4, Et, 9.1; *n*-Pr, −32.5; *s*-Pr, −41.6; *s*-Bu, −62; *t*-Bu, −72.0.

enthalpy of formation of compounds of the general structure $R^1R^2R^3C\text{-}X$ (R^i = H, Me, Et). From the disproportionation reaction

$$\underset{\mathbf{10}}{2(\mathrm{Et})(\mathrm{Me})\mathrm{CH\text{-}OH}} = \underset{\mathbf{11}}{\mathrm{Et_2CHOH}} + \underset{\mathbf{12}}{n\text{-}\mathrm{PrOH}} \qquad (6)$$

and writing

$$\Delta H_f^\circ(\mathbf{10}) = 0.5[\Delta H_f^\circ(11) + \Delta H_f^\circ(12)]$$

we obtain

$$\Delta H_f^\circ(s\text{-BuOH}) = 0.5[(-315.5) + (-272.5)] = 294 \text{ kJ/mol}$$

This value agrees almost perfectly with the experimental one, −295 kJ/mol. In a manner analogous to that of eq 7 we estimate the enthalpy of formation of *s*-$PrNH_2$:

$$\underset{\mathbf{13}}{2\mathrm{Me_2CHNH_2}} = \underset{\mathbf{14}}{\mathrm{Me_3CNH_2}} + \underset{\mathbf{15}}{\mathrm{EtNH_2}} \qquad (7)$$

$$\Delta H_f^\circ(\mathbf{13}) = 0.5[\Delta H_f^\circ(\mathbf{14}) + \Delta H_f^\circ(\mathbf{15})] = 0.5[(-120.9) + (-47.5)] = -84.2 \text{ kJ/mol}$$

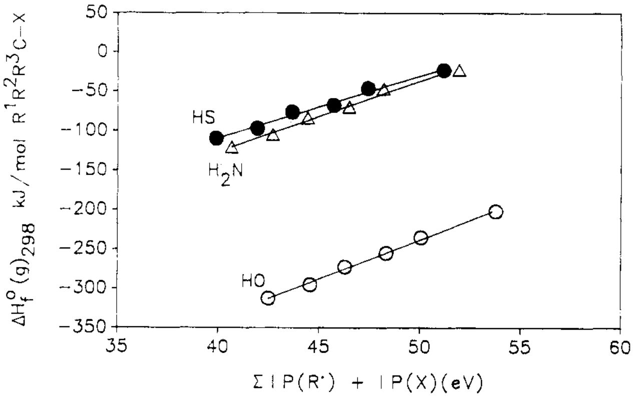

Figure 16. Enthalpies of formation (gas, 298.15 K, kJ/mol) of alcohols, thiols, and amines of the general structure $R^1R^2R^3CX$ (X = OH, SH, NH_2, R^i = H, Me, or Et) plotted as in Figure 15. X = OH: Me, −201.6; Et, −234.8; *n*-Pr, −254.8; *s*-Pr, −272.5; *s*-Bu, −295.0; *t*-Bu, −312.5. X = SH: Me, −22.9; Et, −46.3; *n*-Pr, −67.9; *s*-Pr, −76.2; *s*-Bu, −96.9; *t*-Bu, −109.6. X = NH_2: Me, −23.0; Et, −47.5; *n*-Pr, −70.2; *s*-Pr, 83.8; *s*-Bu, −104.8; *t*-Bu, −120.9. IP(X) (eV): X = $HO^\bullet$, 13.00; X = $HS^\bullet$, 10.37; X = $H_2N^\bullet$, 11.14 (all data from ref 12).

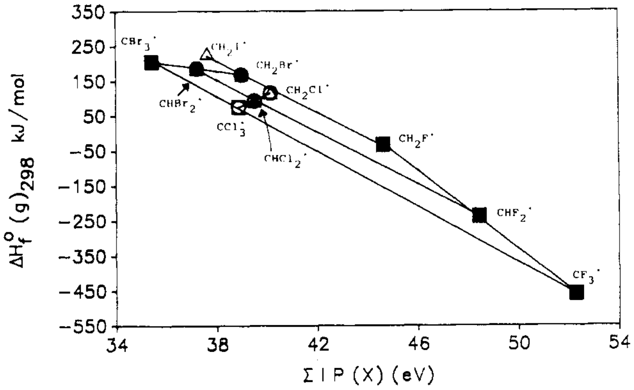

Figure 17. Enthalpies of formation of halogenated methyl radicals (gas, 298.15 K, kJ/mol), plotted against the respective sums of the IP(X,H)'s: $ClCH_2^\bullet$, 115.9; $Cl_2CH^\bullet$, 93.3; $Cl_3C^\bullet$, 75.3; $BrCH_2^\bullet$, 168.2; $Br_2CH^\bullet$, 185.5; $Br_3C^\bullet$, 205.0; $ICH_2^\bullet$, 229.7 (from ref 11); $FCH_2^\bullet$, −33.0; $F_2CH^\bullet$, −237.5; $F_3C^\bullet$, −460.0 (from ref 12).

The experimental value is −83.8 kJ/mol. The predicted value is 0.4 kJ/mol more negative than the experimental one.

If we now take into account the ionization potential of X along with the ionization potentials of $H^\bullet$, $Me^\bullet$, and $Et^\bullet$ in the series $R^1R^2R^3CX$, where X = F, Cl, Br, and I, we obtain the cross correlation in Figure 15. It must be pointed out that if the ionization potential of X had not been included in the sum, we would have missed half of the correlations in Figure 15. An analogous plot is given in Figure 16 for X = OH, SH, and NH_2, but here the lack of thermochemical data for alkyl selenols does not allow an analysis as complete as that in Figure 15. Obviously, the cross correlations are possible only in the case where X involves elements of the same group. Figure 15 constitutes an intra-inter series correlation which could be very informative. The near-parallel lines imply the following: *The effect of a halogen for the enthalpy of formation varies directly proportionally or linearly from one alkyl derivative to another. The effect of an alkyl group on the enthalpy of formation varies in a directly proportional or linear manner from one halogen derivative to another.*

Enthalpies of formation of free radicals also exhibit linear dependence on ionization potentials. In Figure 17 are shown interrelated enthalpies of formation of halogenated methyl radicals. Specifically, these correlations

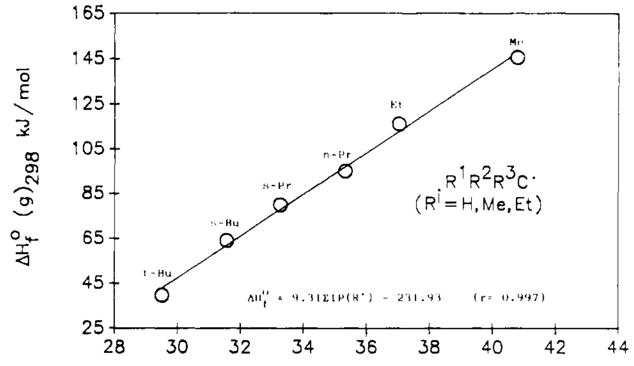

Figure 18. Enthalpies of formation (gas, 298.15 K, kJ/mol) of $R^1R^2R^3C^\bullet$ (R^i = H, Me, or Et) free radicals, plotted against the respective sums of the ionization potentials of the free radicals that correspond to R^i: Me, 145.6; Et, 116.32; *n*-Pr, 94.98; *s*-Pr, 79.91; *s*-Bu, 64.02; *t*-Bu, 39.75 (from ref 13).

involve (a) enthalpies of formation of $XCH_2^\bullet$ (X = F, Cl, Br, and I) versus the sum of the ionization potentials of X and H, (b) enthalpies of formation of $X_2CH^\bullet$ (X = F, Cl, and Br) versus the sum of the respective IP(X,H)'s, (c) enthalpies of formation of $X_3C^\bullet$ (X = F, Cl, and Br) against the sum of IP(X)'s, (d) enthalpies of formation of the series $ClCH_2^\bullet$, $Cl_2CH^\bullet$, and $Cl_3C^\bullet$ versus the sum of the ionization potentials of Cl and H, (e) enthalpies of formation of the series $BrCH_2^\bullet$, $Br_2CH^\bullet$, and $Br_3C^\bullet$ against the sum of IP(Br,H)'s, (f) enthalpies of formation of $FCH_2^\bullet$, $F_2CH^\bullet$, and $F_3C^\bullet$ against the sum of IP(F,H)'s. The data of Holmes and Lossing[11] for $XCH_2^\bullet$ (X = Cl, Br, and I) correlate perfectly with the respective sums of IP(X,H)'s. This is indicative of the (perfect) internal consistency of the data. The value, however, obtained by extrapolation for the enthalpy of formation of $FCH_2^\bullet$, −85.5 kJ/mol, is in serious disagreement with that in the literature,[12] −33 kJ/mol.

Assuming again that the halogen contribution to the enthalpy of formation of halogenated methyl radicals is additive and/or transferable, we can write, for example

$$\underset{\mathbf{16}}{2Cl_2CH^\bullet} = \underset{\mathbf{17}}{CCl_3^\bullet} + \underset{\mathbf{18}}{ClCH_2^\bullet} \qquad (8)$$

and hence

$$\Delta H_f^\circ(\mathbf{16}) = 0.5[\Delta H_f^\circ(\mathbf{17}) + \Delta H_f^\circ(\mathbf{18})] = 0.5(75.3 + 115.9) = 95.6 \text{ kJ/mol}$$

namely, 2.6 kJ/mol higher than the experimental value, 93.3 kJ/mol. Similarly, the estimated enthalpy of formation of $Br_2CH^\bullet$ is 186.6 kJ/mol, i.e., 0.8 kJ/mol higher than the experimental value, 185.8 kJ/mol.

If we now use the estimated value for the enthalpy of formation of $FCH_2^\bullet$, −85.5 kJ/mol, and the literature[12] value for $CF_3^\bullet$, −460 kJ/mol, we estimate, by a scheme analogous to that in eq 8, the enthalpy of formation of $F_2CH^\bullet$ to be −273 kJ/mol. Therefore, the enthalpies of formation of fluorinated free radicals which are perfectly consistent with the values of Holmes and Lossing[11] for the ΔH_f° of halogenated methyl radicals are as follows: $FCH_2^\bullet$, −85.5; $F_2CH^\bullet$, −273; $F_3C^\bullet$, −460 kJ/mol.

Enthalpies of formation of $Me^\bullet$, $Et^\bullet$, *n*-$Pr^\bullet$, *s*-$Pr^\bullet$, *s*-$Bu^\bullet$, and *t*-$Bu^\bullet$ are correlated (Figure 18) with the respective sums of the ionization potentials of $H^\bullet$, $Me^\bullet$, and $Et^\bullet$, analogously to those in Figure 14. As a test of transferability and/or additivity of the H, Me, and Et group contributions to the enthalpy of formation of free alkyl radicals, we consider

$$\underset{\mathbf{19}}{2Me_2CH^\bullet} = \underset{\mathbf{20}}{Me_3C^\bullet} + \underset{\mathbf{21}}{CH_3CH_2^\bullet} \qquad (9)$$

and hence

$$\Delta H_f^\circ(\mathbf{19}) = 0.5[\Delta H_f^\circ(\mathbf{20}) + \Delta H_f^\circ(\mathbf{21})] = 0.5(39.75 + 116.31) = 78.03 \text{ kJ/mol}$$

The experimental[13] value is 79.91 kJ/mol, namely, the predicted value is by 1.88 kJ/mol lower than the experimental one.

The question as to whether the correlations of enthalpies of formation with ionization potentials indicate the implication of dispersion energies in the thermochemical parameters of the compounds involved remains to be answered by the theoreticians. It has been pointed out earlier[7] that ionization potentials of alkyl free radicals provide perhaps the first example of a set of substituent parameters that can be obtained by direct experimental and theoretical methods. In other words, this set of substituent constants is not derived from a specific basis set of kinetic or equilibrium experiments. Therefore they should be devoid of medium effects and certainly should be of more general applicability than the conventional ones. The same can be said for the ionization potentials of halogens and of the radicals $HY^\bullet$, Y = O, S, and NH. It is felt that the ionization potential of any free radical can function as a substituent constant.

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