할로겐화합물의 표준생성열의 계산

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Semiempirical Estimation of Standard Enthalpy of Formation for Halogen Substituted Hydrocarbons

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요 약. 정전기적모델과 결합의 단순한 부가성을 이용하여 아주 극성인 화합물의 표준생설열(ΔH_f°)를 계산하는 간단한 방법을 제안하였다. 이 ΔH_f°에 대한 할로메탄의 bond 기여도는 각각 ΔH_f°(C–F) = –36.44 kcal/mol, ΔH_f°(C–Cl) = –2.57 kcal/mol, ΔH_f°(C–Br) = 5.32 kcal/mol, ΔH_f°(C–I) = 19.18 kcal/mol, and ΔH_f°(C–H) = –3.61 kcal/mol 로 얻어졌고 이 값들과 정전기적 에너지들로부터 계산한 ΔH_f°는 실험치와 잘 일치함을 보였다.

ABSTRACT. By using electrostatic model and simple bond additivity scheme a reasonable and simple method was developed for the estimation of standard enthalpy of formation (ΔH_f°) of very polar compounds.

The bond contributions to the enthalpy of formation for halomethanes were; ΔH_f°(C–F) = –36.44 kcal/mole, ΔH_f°(C–Cl) = –2.57 kcal/mole, ΔH_f°(C–Br) = 5.32 kcal/mole, ΔH_f°(C–I) = 19.18 kcal/mole, and ΔH_f°(C–H) = –3.61 kcal/mole, respectively. Using these values and calculated electrostatic energies, the estimated ΔH_f° values were estimated and found to be in good agreement with observed values.

INTRODUCTION

The entropy and enthalpy of formation are important properties of chemical compounds for the calculation of equilibrium constants. They are also very useful for the estimation of kinetic parameters.[1] While the entropy of most compounds can be estimated with reasonable accuracy (± 0.5 e.u.) from the structural and spectroscopic data or from the known entropy of structually analogous compounds,[1] the estimation of ΔH_f° is relatively difficult especially for very polar compounds such as halogen or oxygen substituted compounds.

An exact quantum mechanical calculation of ΔH_f° for polyatomic molecules is presently impossible, and the situation will not change in near future. There have been many attempts for the semiempirical estimation of ΔH_f°. A simple bond additivity method[2], although very

simple, only gave rough estimation of $\Delta H_f{}^\circ$. The next higher correction scheme is the group additivity method[3] which includes the next nearest neighbor interaction. Although it gives a reasonable agreement with experimental values for most hydrocarbon compounds, it still doesnot account for the non-bonded interaction, *e. g. cis-, trans*-compounds give same $\Delta H_f{}^\circ$, and still does not give accurate results for halogen substituted compounds. Most of all, the necessary data base for various groups increases enormously, *i. e.* too many data base is needed. Some modified versions of bond additivity method have been suggested.[4] However, the results are either inaccurate or too many parameters have to be used.

Recently Benson and Luria[5] suggested simple electrostatic model to account for the stability of branched hydrocarbons relative to normal hydrocarbons, and gave very simple scheme for the estimation of $\Delta H_f{}^\circ$ for hydrocarbon compounds.

An estimation of $\Delta H_f{}^\circ$ for halogen substituted hydrocarbons is important in several aspects; 1) A general experimental difficulty in calorimetric measurements of $\Delta H_f{}^\circ$ for halogen compounds leads to the erroneous results for $\Delta H_f{}^\circ$ values. 2) There is practical usefulness of the $\Delta H_f{}^\circ$ values for the estimation of equilibrium and kinetic parameters of the halocarbon compounds, especially in air- and water-pollution of many chloro- and fluoro-substituted commercial products. 3) There always have been large discrepancies between $\Delta H_f{}^\circ$ values calculated by semiempirical method and $\Delta H_f{}^\circ$ values obtained experimentally. It seems worth looking into the origin of the discrepancies.

Choo and John[6] recently applied Benson and Luria's method to the chlorine and fluorine substituted hydrocarbons. However the calculation from the fixed charge model (Benson & Luria) did not give meaningful results for halogen compounds. When using fixed charges for halogens in order to estimate $\Delta H_f{}^\circ$ Values for the series of halogen substituted methanes, *e. g.* $CH_3X\text{-}CH_2X_2\text{-}CHX_3\text{-}CX_4$ (X=halogen), corrections should be made for each substituted chlorine atoms in a given compound. They thus believe that the charges withdrawn from carbon atoms by halogen are gradually decreased with the substituted halogen atoms. Furthermore the fixed charge model could not explain the dipole moments of halogen substituted compounds.

Sometime ago Smith and coworkers[7] reported simple scheme for the calculation of induced formal charges. From the known values of bond polarizability and dipole moment data they could successfully calculate the dipole moments of halomethanes. For the calculation of charges their method was used in the present work.

In this paper, an attempt was made to find a reasonable model to account for the origin of deviations in bond additivity method, and suggest simple and more accurate method for the estimation of $\Delta H_f{}^\circ$ for halogen compounds.

ELECTROSTATIC MODEL

The basic assumption in the present author's is that the enthalpy of formation, $\Delta H_f{}^\circ$, can be divided into two major parts; the nonelectrostatic bond contributions and the contribution of bonded and nonbonded electrostatic interaction *i. e.* for example,

$$\Delta H_f{}^\circ (CH_3Cl) = \Delta H_f{}^\circ (C\text{-}Cl) + 3\Delta H_f{}^\circ (C\text{-}H) + E_{el}$$

the electrostatic energies may be calculated from the charge–charge interaction (Coulombic) of the induced charges. The charges are assumed to be point charges located on the centers of atoms. The induced charges can be estimated with a method by Smith and coworkers using the bond polarizability and dipole moment data

from the literatures[7]. Then, E_{el} may be calculated as

$$E_{el} = \sum_{i=1}^{n} \sum_{j=i+1}^{n} Q_i Q_j / r_{ij}$$

where Q_i, Q_j are the charges on ith and jth atom, and r_{ij} is their distance apart. All the distances for specific bonds are assumed to be same in different compounds and carbon atoms are assumed to have tetrahedral geometry. *Table* 1 shows the parameters used in the calculation. From the calculated E_{el} and known ΔH_f° values it was possible to obtain the best values for nonelectrostatic bond contribution.

CHARGE CALCULATION

The moment induced in a system by a field of strength E is

$$\mu = \alpha E$$

where α is the polarizability tensor.

Then, Q_a^b, the net charge on atom due to the polarization of the electron pair $a-b$ for the electron cloud of the two bonding electrons in a-b bond, can be given,

$$-Q_a^b R_{ab} = (b_1)_{ab}\left(\frac{Z_a^\circ e}{R_a^2} - \frac{Z_b^\circ e}{R_b^2}\right) \tag{1}$$

where R_{ab} is the internuclear distance and $(b_1)_{ab}$ the longitudinal polarizibility of $a-b$, Z_a° and Z_b° are the effective nuclear charges of a and b, respectively, and R_a and R_b are the covalent radii of a and b.

The principal assumption in equation (1) is

Table 1. The parmaetsers for the calculation of charges.

Compound	μ(debye)	R_{CX}, Å	β_{XC}^c	γ_{XC}^d
CH_3F	1.85[a]	1.33[b]	0.2536	−1.5325
CH_3Cl	1.87[a]	1.77[b]	0.7053	−1.5128
CH_3Br	1.81[a]	1.94[b]	0.9064	−1.4719
CH_3I	1.62[a]	2.13[b]	1.2883	−1.4068
CH_4	0	1.093	0.1254	0

[a]CRC Handbook of Chemistry and Physics.　[b]S. W. Benson, "Thermochemical Kinetics," 2 nd Ed., P. 302 Table A-14.　$^c\beta_{ab} = \dfrac{\beta_b^a}{1+\beta_a^b}$　$^d\gamma_{ab} = \dfrac{\alpha_{ab}}{1+\beta_a^b}$　(uint is 10^{-10} esu).

Table 2. The values of β_a^b and β_b^a.

Bond a-b	$b_1 \times 10^{24}$	R_a, Å	R_b, Å	β_a^b	β_b^a
C–C	1.88	0.771	0.771	0.718[a]	0.718
C–F	0.96	0.771	0.640	0.401	0.581
C–Cl	3.67	0.771	0.990	1.23	0.744
C–Br	5.04	0.771	1.14	1.55	0.710
C–I	8.09	0.771	1.33	2.27	0.762
C–H	0.79	0.771	0.30	0.434	2.46

[a]Smith and Mortensen obtained 0.43 for this value. see *J. Amer. Chem. Soc.*, 78, 3932 (1956).

that a bond dipole moment may be represented by equal and opposite net charges located on the atomic nuclei.

With Slater's screening factor[8] and rearrangement of equation (1) given above, we obtain

$$Q_a{}^b = \alpha_{ab} + \beta_b{}^a e_b - \beta_a{}^b e_a \qquad (2)$$

where e_a is the net charge on atom a (sum of net charge contributions from all bonds joined to a).

$$\alpha_{ab} = -\frac{(b_1)_{ab}e}{R_{ab}}\left(\frac{Z_a{}^\circ}{R_a{}^2} - \frac{Z_b{}^\circ}{R_b{}^2}\right)$$

$$\beta_b{}^a = \frac{0.35(b_1)_{ab}}{R_{ab}R_b{}^2}, \quad \beta_a{}^b = \frac{0.35(b_1)_{ab}}{R_{ab}R_a{}^2}$$

Some of the $(b_1)_{ab}$, $\beta_a{}^b$ and $\beta_b{}^a$ values are tabulated in *Table* 2. α_{ab} can be calculated from the known methyl halide electric dipole moment. From the values α_{ab}, $\beta_b{}^a$, and $\beta_a{}^b$ and the necessary condition that the sum(including the sign) of the total charges in a molecule must be zero *i.e.* $\sum_i e_i = 0$, the total net charges at each atom can be calculated with equation (2).

RESULTS AND DISCUSSION

Formal Charges of Halomethanes. The calculated formal charges of halomethanes are shown in *Table* 3. From the table it is evident that the net charges withdrawn by halogen atoms are gradually decreased by increasing the number of substituted halogen atoms. (*cf.* column of the table) This fact is in qualitative agreement with Choo and John's result that the charges of halogen atoms can not have fixed values to account for the $\Delta H_f{}^\circ$ of halogen compounds. For the same type of compounds (*e. g.* CH₃X, CH₂X₂, *etc.*) the negative charges on halogen atoms decreased in the order, F>Cl> Br>I, as expected from the electronegativity of the halogen atoms. It is also interesting to note that the less electronegative halogenatoms

can have positive formal charges depending on properties of other substituted halogen atoms on the same carbon atom (*e. g.* I in CF_2I_2, $CHFI_2$ *etc.*)

Enthalpy of Formation, $\Delta H_f{}^\circ$. From the calculated formal charges and the bond angle and bond distances the coulombic electrstatic energies can be calculated. Before using the electrostatic energy for the estimation of $\Delta H_f{}^\circ$, the $\Delta H_f{}^\circ$'s of several bond conserving reactions werefirst calculated. In this model it was assumed that the deviation from the bond additivity came from the electrostatic energy. Therefore, several bond conserving reactions, *e. g.*

$$CH_4 + CH_2Cl_2 = 2CH_3Cl$$

were selected in order to check the validity of the assumption. The observed heats of reactions ($\Delta H_r{}^\circ$) and calculated electrostatic energy differences (ΔE_{el}) for several bond conserving reactions are listed in *Table* 4 (all the bond angles are assumed to be those of tetrahedral structure).

$\Delta H_r{}^\circ$ and ΔE_{el} values for these reactions agree reasonably with each other, proving that this model is a fairly good one for the estimation of $\Delta H_f{}^\circ$ for halogen compounds. Use of correct geometries of the compounds may improve the results of calculation.

The contributions of the nonelectrostatic bonds to the heats of formation were obtained by the following method.

For example, $\Delta H_f{}^\circ$ for C-F bond can be esti mated from the relationship,

$$\Delta H_f{}^\circ(CF_4) = 4\Delta H_f{}^\circ(C\text{-}F) + E_{el}$$

using the data $\Delta H_f{}^\circ(CF_4) = -223.0$ kcal/mole and $E_{el} = -77.24$ kcal/mole for CF_4 molecule, one can get

$$\Delta H_f{}^\circ(C\text{-}F) = \frac{\Delta H_f{}^\circ(CF_4) - E_{el}}{4}$$

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Table 3. The calculated charges on various halomethanes.

Compound	X	F	Cl	Br	I
CH₃X	C	0.9403	0.7269	0.6447	0.5280
	H	0.1179	0.0911	0.0809	0.0662
	X	-1.294	-1.000	-0.8874	-0.7266
CH₂X₂	C	1.7436	1.1368	0.9608	0.7350
	H	0.2186	0.1426	0.1205	0.0922
	X	-1.0904	-0.7110	-0.6009	-0.4597
CHX₃	C	2.4375	1.4003	1.1484	0.8458
	H	0.3057	0.1756	0.1440	0.1061
	X	-0.9144	-0.5253	-0.4308	-0.3173
CX₄	C	3.0432	1.5836	1.2728	0.9144
	X	-0.7608	-0.3959	-0.3182	-0.2286
CF₂X₂	C	2.0874		1.8098	1.4394
	F	-1.0031		-1.0735	-1.1674
	X	-0.0406		0.1686	0.4477
CHFX₂	C		1.6340	1.4023	1.0987
	H		0.2049	0.1759	0.1378
	F		-1.1181	-1.1768	-1.2539
	X		-0.3604	-0.2007	0.0087
CHF₂X	C		1.9581	1.7868	1.5309
	H		0.2455	0.2241	0.1920
	F		-1.0359	-1.0793	-1.1442
	X		-0.1318	0.1477	0.5655
CFX₃	C		1.8016	1.4972	1.1239
	F		-1.0756	-1.1528	-1.2475
	X		-0.2420	-0.1148	0.0412

**all units are 10^{-10} esu

Table 4. The Calculated (E_{el}) and observed ($\Delta H_r°$) values forbond conserved reactions.

Reaction	$\Delta H_r°$	ΔE_{el}
$CH_4+CH_2Cl_2=2CH_3Cl$	-0.57	-0.86
$CH_4+CCl_4=2CH_2Cl_2$	-1.72	-1.60
$CH_2Cl_2+CCl_4=2CHCl_3$	-0.39	-0.16
$CH_3Cl+CHCl_3=2CH_2Cl_2$	-0.78	-0.29

**unit is kcal/mole

$$= \frac{-223.0-(-77.24)}{4}$$

$= -36.44$ kcal/mole

$\Delta H_f°$'s for C-Cl and C-Br bonds were obtained by the same method with the results $\Delta H_f°$ (C-Cl) = -2.57 kcal/mole, $\Delta H_f°$ (C-Br) = 5.32 kcal/mole. $\Delta H_f°$ (C-H) can be estimated from $\Delta H_f°$ and E_{el} data of several fluoro-, chloro-, and bromo-methanes. From these calculations, $\Delta H_f°$ (C-H) = -3.61 kcal/mole was chosen as the best fit value. Estimation of the bond enthalpy for C-I poses a little problem since there are no reported data of $\Delta H_f°$ for CI_4. Therefore, $\Delta H_f°$ (C-I) had to be estimated from the $\Delta H_f°$

Table 5. Calculated and observed ΔH_f° for polysubstituted halomethanes.

Compound	E_{el}	ΔH_f° (obsd)	ΔH_f°(calcd)	Δ	Ref.
CH_3F	− 11.78	− 56.8±2	− 59.05	2.2±2	a
CH_2F_2	− 29.78	−108±1	−109.88	1.9±1	a
CHF_3	− 52.04	−166±1	−164.97	1.0±1	a
CF_4	− 77.24	−223	−223	0	b
CH_3Cl	− 4.76	− 19.6	− 18.16	−1.44	c
CH_2Cl_2	− 8.66	− 22.81	− 21.02	−1.79	b
$CHCl_3$	− 12.27	− 24.2	− 23.59	−0.61	b
CCl_4	− 15.72	− 26	− 26	0	d
CH_3Br	− 3.26	− 9.02	− 8.8	−0.22	b
CH_2Br_2	− 5.41	− 1.0	− 2.0	1	b
$CHBr_3$	− 7.37	6.0	4.98	1.02	b
CBr_4	− 9.26	12.0	12	0	b
CH_3I	− 1.88	4.0	6.47	−2.47	d
CH_2I_2	− 2.74	28.2	28.40	−0.2	b
CHI_3	− 3.55	50.4	50.40	0	b
CI_4	− 4.35		72.37		
$CHClF_2$	− 34.92	−115.6±1	−113.98	−1.6±1.4	a
$CClF_3$	− 55.39	−166	−167.28	1.28	a
CCl_2F_2	− 39.12	−118	−117.14	−0.86	d
$CFCl_3$	− 26.33	− 70	− 70.48	0.48	d
$CBrF_3$	− 51.53	−155.1	−155.5	0.4	b
CBr_2Cl_2	− 12.51	− 7.0	− 7.02	0.02	b
$CClBr_3$	− 10.88	3.0	2.5	0.5	b
$CHBrCl_2$	− 10.63	− 14.0	− 14.7	0.07	b
$CHBr_2Cl$	− 8.99	− 5.0	− 4.54	−0.46	b
$CHBr_2I$	− 6.21	20.0	20.0	0	b
CH_2BrCl	− 7.02	− 12.0	− 11.5	−0.5	b
CH_2BrI	− 4.1	− 12.0	13.18	−1.18	b
CH_2ClI	− 5.68	3.0	3.71	−0.71	b

**All units are in kcal/mole. (a) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", London, Academic Press, 1976; (b) D. R. Stull, E. F. Westrum and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", N. Y., John Wiley, 1969; (c) S. W. Benson, "Thermochemical" Kinetics, John Wiley and Sons, 1976; (d) Saul Patai, Ed., "The Chemistry of the Carbon-Halogen Bond Part 2", John Wiley and Sons, 1973.

of Iodomethanes using the ΔH_f° (C-H) value obtained previously. the value of ΔH_f° (C-I) = 19.18 kcal/mole.

Using the bond enthalpies thus obtained and calculated electrostatic energies of each compound, it was possible to estimate the heats of formation of various halomethane compounds. The results are listed in *Table* 5. The calculated values in the table are in excellent agreement with experimentally observed values. It is important to note that simple geometries (tetrahedral carbon atoms and fixed C-X bond distances) were used for the calculation of E_{el}. With correct geometrical data the agreement can be improved further.

Dipole Moment Calculation. The calculated charges on atoms in molecules were checked by comparing calculated and obsered electric dipole

Table 6. The calculated and observed dipole mome nt of halomethanes.

Compound	μ(calcd)[a]	μ(obsd)*	Ref.
CH_3F	1.85	1.85	a
CH_2F_2	1.95	1.97	a
CHF_3	1.55	1.65	a
CF_4	0	0	
CH_3Cl	1.87	1.87, 1.86	a, b
CH_2Cl_2	1.63	1.60	a
$CHCl_3$	1.12	1.01	a
CCl_4	0	0	
CH_3Br	1.81	1.81, 1.82	a, b
CH_2Br_2	1.45	1.43	a
$CHBr_3$	0.99	0.99	a
CBr_4	0	0	
CH_3I	1.62	1.62, 1.71	a, b
CH_2I_2	1.25		
CHI_3	0.79		
CI_4	0		
$CHClF_2$	1.66	1.42	a
$CHCl_2F$	1.4	1.29	a
CH_2ClF	71.5	1.28	a

*unit in Debye.   (a) CRC Handbook of Chemistry and Physics; (b) The Chemist's Companion, "A Handbook of practical Data, Techniques, and References," John Wiley and Sons, 1972.

moments of some halogen substituted methanes. The results of calculation are shown in Table 6, which show a reasonable agreement with observed values.

In addition to the above information (ΔH_f°, dipole moments), the calculated charges on atoms in molecule can be used to predict the order of reactivity of many polar reactions quantitatively.

It would be possible to extend charge calculation in the present work to the other very polar compounds, such as nitro- and oxygen substituted ones. Such a study is being carried out by the authors.

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