

The link between the ionization potential and heat of formation for organic homologous compounds

Chenzhong Cao*

School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, People's Republic of China

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ABSTRACT: Based on the relationship between the heat of formation and the change of valence electronic energy in the formation of a compound from its component atoms, and combined with the relationship between the first ionization potential and the average valence electronic energy, the direct link of ionization potential, I_p , with the heat of formation, ΔH_f^0 , was deduced for organic homologous compounds, that is,

$$I_p \cdot N_{ve,m} = a + b \left[\sum SVEE_x - \Delta H_f^0 \right] + cR_m$$

where $N_{ve,m}$ is the number of valence electrons in molecule, $SVEE_x$ is the sum of valence electronic energy of isolated atoms forming the molecule, the term $(\sum SVEE_x - \Delta H_f^0)$ expresses the initial-state effect of the molecule, and the symbol R_m represents its final-state effect (polarizability effect). The above equation was confirmed by the correlations between the ionization potentials and the heat of formation of alkanes, alkenes, monosubstituted alkanes RY (Y = OH, NH₂, SH, Cl, Br, and I), in which all the expressions have good correlations with correlation coefficients more than 0.9990. With the obtained correlation equations, the ionization potentials of some monosubstituted alkanes were predicted from their experimental heats of formation. The result provides a new insight into the intercorrelation between the ionization potential and the heat of formation for organic homologous compounds. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: ionization potential; heat of formation; valence electronic energy; alkane; alkene; monosubstituted alkane

INTRODUCTION

It is well known that the property of a compound is dominated by its molecular structure. When a new organic compound was synthesized and its diverse physicochemical properties (such as melting point (mp), boiling point (bp), heat of formation, and ionization potential, etc.) were measured, an interesting as well as a fascinating doubt would arise. That is, how does a kind of physicochemical property associate with another one? The investigation of this subject helps us not only to understand the correlation between the molecular structure and the property or activity, but also to predict the property of a more expensive or time-consuming test from that of less expensive tests and measurements.¹ Katritzky *et al.*¹ observed a pair correlation between the properties (mp, bp, refractive index, molar volume (MV), and density), and got the results that no pair within the five properties is highly intercorrelated for all the three kinds

of compounds, aldehydes, amines, and ketones. Needham *et al.*² investigated the correlations among the eight physical properties of 74 normal and branched alkanes, in which the eight properties were bp, molar volume (MV), molar refraction (MR), heat of vaporization (HV), surface tension (ST), mp, critical temperature (T_c), and critical pressure (P_c). It was observed that some pairs of properties had good correlations, such as the pair of bp and T_c , bp and HV, MV and MR, etc., but the correlations were bad between the mp and other seven properties. However, we think, the intercorrelations must exist among these physicochemical properties originating from a same molecular structure. Perhaps, some of the correlations among those properties are easily observed (e.g., the density D , molar volume MV, and the molar mass M have the relationship of $D=M/MV$ for liquid compounds), while others are difficult to be searched for.

Commonly, it was viewed that the ionization potential of a molecule reflects its valence electronic energy in the highest occupation molecule orbital (HOMO), and the heat of formation scales the energy change during the formation of a molecule from its component atoms. Thus, an interesting topic is put forward, that is, how to link the

*Correspondence to: C. Cao, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, 411201, People's Republic of China.
E-mail: czcao@hust.edu.cn

heat of formation with the first ionization potential for a compound. Jones *et al.*³ measured the ionization potential (Ip) of thioformaldehyde and evaluated its heat of formation. Shapiro *et al.*⁴ and Kohn *et al.*⁵ determined the heat of formation of dichlorocarbene CCl₂ by means of measuring its ionization potential. McAllister *et al.*⁶ and Burkey *et al.*⁷ also evaluated the heat of formation of PH₂ and α -aminoalkyl radicals from the experimental ionization potentials. Recently, Thanikaivelan⁸ used quantum chemistry method to calculate the ionization potential of alkanes (C₂–C₈) and investigated the correlation between the ionization potential and the heat of formation. All the meaningful works mentioned above indicate that there seems to be a direct link between the ionization potential and the heat of formation for a series of organic compounds, but they did not obtain a general relationship for this link. This paper intends to investigate this link.

THE LINK OF THE IONIZATION POTENTIAL AND THE HEAT OF FORMATION

A compound A_nB_m is formed from the isolated atoms A and B, as shown in Eqn (1):



where *n* and *m* are the number of atoms A and B, respectively. What we are concerned about Eqn (1) is how to correlate the ionization potential of the molecule A_nB_m with its heat of formation and the properties of the isolated atoms A and B. Based on the viewpoint of chemistry, the heat of formation of molecule A_nB_m mainly depends on the energy difference between the valence electrons of A_nB_m and those of the corresponding atoms A and B. According to Parr's⁹ definition, electronegativity χ is the negative value of the chemical potential μ of an atomic or a molecular electron cloud [see Eqn (2)].

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_v \quad (2)$$

where *E* is the exact Hohenberg and Kohn energy functional for an *N*-electron system characterized by an external potential *v*.

From Eqn (2), the total energy of all valence electrons in an atom or a molecule can be calculated with Eqn (3).

$$SVEE = -\int_0^{N_{ve}} \chi dN = \int_{E_0}^{E_{N_{ve}}} dE \quad (3a)$$

or

$$SVEE = -\chi N_{ve} = E_{N_{ve}} - E_0 \quad (3b)$$

in which SVEE is the sum of valence electronic energy, *N*_{ve} is the valence electron number of an atom or a molecule. Allen¹⁰ suggested that 'electronegativity is the

average one-electron energy of the valence-shell electrons in ground-state free atoms', which can be expressed as shown in Eqn (4).

$$\chi = -\frac{\sum n_i E_i}{\sum n_i} \quad (4)$$

where *E_i* is the energy of *i*th valence electron and *n_i* is the number of the valence electron with energy *E_i*. Combining Eqn (3b) with Eqn (4), we can get Eqn (5):

$$SVEE = -\chi N_{ve} = -\frac{\sum n_i E_i}{\sum n_i} N_{ve} \quad (5)$$

For the ground-state neutral atom, *N*_{ve} = $\sum n_i$, thus, SVEE = $\sum n_i E_i$. For the ground-state molecule, the term ($\sum n_i E_i$)/($\sum n_i$) of Eqn (5) represents the average one-electron energy of the valence electrons, which is expressed with symbol *E*_{avm} in this work.

If the symbols *N*_{ve,x} and *N*_{ve,m} are employed to represent the number of valence electrons in atom A (or B) and molecule A_nB_m, respectively, and the symbols SVEE_x and SVEE_m for the sum of valence electronic energy of isolated atom A (or B) and the molecule A_nB_m, respectively, the SVEE_x and SVEE_m will be calculated with Eqns (6), (7).

$$SVEE_x = -\left[\frac{\sum n_i E_i}{\sum n_i}\right]_x N_{ve,x} = -\left[\sum n_i E_i\right]_x \quad (6)$$

$$SVEE_m = -\left[\frac{\sum n_i E_i}{\sum n_i}\right]_m N_{ve,m} = -E_{avm} N_{ve,m} \quad (7)$$

in which, *N*_{ve,x} = ($\sum n_i$)_x, *N*_{ve,m} = $\sum N_{ve,x}$. That is, for the molecule A_nB_m, *N*_{ve,m} = *nN*_{ve,A} + *mN*_{ve,B}.

Therefore, the heat of formation ΔH_f^0 of compound A_nB_m in Eqn (1) can be approximately evaluated with Eqn (8), ignoring the inner-shell electron energy.

$$\begin{aligned} \Delta H_f^0 &= SVEE_m - \sum SVEE_x \\ &= -E_{avm} \times N_{ve,m} - [-n(\sum n_i E_i)_A \\ &\quad - m(\sum n_i E_i)_B] \end{aligned} \quad (8)$$

in which $\sum SVEE_x = -[n(\sum n_i E_i)_A + m(\sum n_i E_i)_B]$. Equation (8) can also be expressed as Eqn (9).

$$E_{avm} N_{ve,m} = [n(\sum n_i E_i)_A + m(\sum n_i E_i)_B] - \Delta H_f^0 \quad (9)$$

It is Eqn (9) that correlates the total energy of valence electrons in molecule A_nB_m with its heat of formation and the total energy of valence electrons in the corresponding isolated atoms A and B, with which the average one-electron energy of the valence electrons (*E*_{avm}) for the molecule A_nB_m can be calculated.

Jolly^{11,12} even pointed out that 'core electron binding energies can be used to establish bench marks for the comparison of valence-shell ionization potentials', and 'lone-pair ionization potential and the corresponding core binding energies are linearly correlated only for sets of

very similar molecules'. If we apply this thesis to the organic homologous compounds and further postulate that the first ionization potentials (I_p) of the homolog are proportional to their average one-electron energy of the valence electrons of the corresponding molecules, that is, $I_p = a_0 E_{avm}$, we can get the Eqn (10) from Eqn (9).

$$I_p \cdot N_{ve,m} = a_0 [n(\sum n_i E_i)_A + m(\sum n_i E_i)_B] - \Delta H_f^0 \quad (10)$$

In fact, the further studies of Aitken¹³ and Cao¹⁴ showed that the core-ionization energy or first ionization potential is dominated by two factors, the initial-state effect and the final-state effect (polarizability effect). It means that the Eqn (10) should be modified as Eqn (11).

$$\begin{aligned} I_p \cdot N_{ve,m} &= a + b [n(\sum n_i E_i)_A + m(\sum n_i E_i)_B] \\ &\quad - \Delta H_f^0 + c R_m \\ &= a + b(\sum SVEE_x - \Delta H_f^0) + c R_m \quad (11) \end{aligned}$$

$$\begin{aligned} I_p \cdot N_{ve,m} &= -11.1130(\pm 8.4611) + 0.6382(\pm 0.0036)(\sum SVEE_x - \Delta H_f^0) \\ &\quad + 42.8569(\pm 7.6324)GMPEI \\ R &= 0.9999, S = 1.70 \text{ eV}, n = 21, F = 66248.24, R_{cv} = 0.9998, S_{cv} = 2.06 \text{ eV} \end{aligned} \quad (13)$$

in which the term $(\sum SVEE_x - \Delta H_f^0)$ expresses the initial-state effect of the molecule $A_n B_m$, the symbol R_m represents its final-state effect (polarizability effect), and a , b , and c are the coefficients. Thus, Eqn (11) provides a direct link of the ionization potential with the heat of formation for organic homologous compounds.

CORRELATION BETWEEN THE IONIZATION POTENTIAL AND HEAT OF FORMATION

Alkane

To verify the rationality of Eqn (11), this paper starts with alkanes. This selection has three advantages: (i) the ionization potentials and heats of formation of many alkanes had been measured experimentally; (ii) all the chemical bonds in alkane molecule are σ bonds and no functional groups exist in the molecule; (iii) the final-state effect (polarizability effect) of alkane can be quantified with the Geometric Mean Polarizability Effect Index (GMPEI) proposed by Cao,¹⁴ and thus the R_m of Eqn (11)

$$\begin{aligned} I_p \cdot N_{ve,m} &= 43.3938(\pm 2.3749) + 0.6752(\pm 0.0035)(\sum SVEE_x - \Delta H_f^0) \\ &\quad - 24.3280(\pm 1.0363)GMPEI_\pi \\ R &= 0.9997, S = 2.17 \text{ eV}, n = 22, F = 18391.22, R_{cv} = 0.9996, S_{cv} = 2.64 \text{ eV} \end{aligned} \quad (14)$$

can be displaced by GMPEI directly.

The dataset used in this work was obtained as follows. The experimental ionization potentials I_p s and heats of formation ΔH_f^0 s of alkanes were taken from the

literature,¹⁵ which was scaled with the unit eV (1eV = 96.49 kJ/mol). The GMPEI was calculated with Cao's¹⁴ method. The $\sum SVEE_x$ was computed according to the molecular component. Take CH_4 for a calculation example. It has one carbon atom with four valence electrons ($2s^2 2p^2$) and four hydrogen atoms bearing one valence electron ($1s^1$). The energies of carbon atomic 2s and 2p electrons are 16.6 and 11.3 eV, respectively, and that of 1s electron of hydrogen atom is 13.6 eV.¹⁶ Hence, the $\sum SVEE_x$ of CH_4 is,

$$\begin{aligned} \sum SVEE_{CH_4} &= (16.6 \times 2 + 11.3 \times 2) \times 1 + 13.6 \times 4 \\ &= 110.2(\text{eV}) \end{aligned} \quad (12)$$

Using the above method, the obtained I_p , ΔH_f^0 , GMPEI, and $\sum SVEE_x$ values of some alkanes are listed in Table 1.

Equation (13) is of good correlation. The average absolute error between the experimental and calculated ionization potential (see Table 1) is only 0.042 eV.

The cross-validation was also carried out with the leave-one-out method and the obtained result (correlation coefficient $R_{cv} = 0.9998$ and standard error $S_{cv} = 2.06$ eV) showed that the Eqn (13) has good stability and predictability, with which the average absolute error between the experimental and the predicted ionization potential is 0.067 eV.

Alkene

The alkenes are different from alkanes in that the first ionization takes place in the π bond. The final-state effect (polarizability effect) mainly resulted from those substituted alkyls attached to the π bond. Therefore, the polarizability effect R_m of Eqn (11) should be displaced with the GMPEI of π bond ($GMPEI_\pi$) of alkene.¹⁴ Using the experimental ionization potentials and heats of formation of alkenes in Table 2, we got correlation expression (14):

The statistical correlation of Eqn (14) is also good. The average absolute error between the experimental and calculated ionization potential (see Table 2) with Eqn (14) is only 0.066 eV. The cross-validation was also carried out

Table 1. The I_p , ΔH_f^0 , GMPEI, and $\Sigma SVEE_x$ values of some alkanes

No.	Alkane ^a	$I_{p_{exp.}}$ (eV) ^b	$\Sigma SVEE_x$ (eV)	ΔH_f^0 (eV) ^b	GMPEI ^c	$I_{p_{calc.}}$ (eV) ^d
1	1	12.61	110.20	-0.77	1.0000	12.82
2	2	11.56	193.20	-0.87	1.1405	11.54
3	3	10.95	276.20	-1.08	1.2187	10.90
4	4	10.53	359.20	-1.30	1.2694	10.51
5	2m3	10.57	359.20	-1.39	1.2807	10.54
6	5	10.28	442.20	-1.52	1.3052	10.25
7	2m4	10.32	442.20	-1.59	1.3177	10.27
8	22mm3	10.20	442.20	-1.74	1.3360	10.30
9	6	10.13	525.20	-1.73	1.3322	10.06
10	2m5	10.12	525.20	-1.81	1.3441	10.08
11	3m5	10.08	525.20	-1.78	1.3469	10.08
12	22mm4	10.06	525.20	-1.93	1.3652	10.10
13	23mm4	10.02	525.20	-1.85	1.3576	10.09
14	7	9.93	608.20	-1.94	1.3533	9.92
15	8	9.80	691.20	-2.16	1.3703	9.80
16	2m7	9.84	691.20	-2.23	1.3803	9.81
17	224mmm5	9.86	691.20	-2.32	1.4108	9.84
18	2233mmmm4	9.80	691.20	-2.34	1.4359	9.86
19	9	9.71	774.20	-2.37	1.3844	9.71
20	10	9.65	857.20	-2.59	1.3963	9.64
21	11	9.56	940.2	-2.81	1.4064	9.57

^a m, methyl.; for example, 3m⁵ represents 3-methylpentane.^b Taken from Ref. 15.^c Calculated with the method of Ref. 14.^d Calculated with Eqn (13).**Table 2.** The I_p , ΔH_f^0 , GMPEI _{π} and $\Sigma SVEE_x$ values of some alkenes

No.	Alkene	$I_{p_{exp.}}$ (eV) ^a	$\Sigma SVEE_x$ (eV)	ΔH_f^0 (eV) ^a	GMPEI _{π} ^b	$I_{p_{calc.}}$ (eV) ^c
1	Ethylene	10.5138	166.00	0.54	1	10.90
2	Propene	9.73	249.00	0.21	1.5103	9.70
3	1-Butene	9.55	332.00	0.00	1.5951	9.53
4	<i>cis</i> -2-Butene	9.11	332.00	-0.07	2.1405	8.98
5	<i>trans</i> -2-Butene	9.1	332.00	-0.12	2.1405	8.98
6	Isobutene	9.239	332.00	-0.18	1.9604	9.17
7	1-Pentene	9.51	415.00	-0.22	1.6228	9.48
8	<i>cis</i> -2-Pentene	9.01	415.00	-0.29	2.2344	8.98
9	<i>trans</i> -2-Pentene	9.04	415.00	-0.33	2.2344	8.98
10	2-Methyl-1-butene	9.12	415.00	-0.36	2.0431	9.14
11	3-Methyl-1-butene	9.52	415.00	-0.29	1.6796	9.43
12	2-Methyl-2-butene	8.69	415.00	-0.43	2.6765	8.63
13	1-Hexene	9.44	498.00	-0.45	1.6469	9.44
14	<i>cis</i> -2-Hexene	8.97	498.00	-0.54	2.2699	9.02
15	<i>trans</i> -2-Hexene	8.97	498.00	-0.56	2.2699	9.02
16	2-Methyl-1-pentene	9.08	498.00	-0.62	2.0769	9.15
17	4-Methyl-1-pentene	9.45	498.00	-0.53	1.6225	9.46
18	2-Ethyl-1-butene	9.06	498.00	-0.58	2.1259	9.12
19	2,3-Dimethyl-1-butene	9.07	498.00	-0.65	2.1259	9.12
20	2,3-Dimethyl-2-butene	8.27	498.00	-0.71	3.2810	8.34
21	1-Octene	9.43	664.00	-0.84	1.6657	9.41
22	1-Decene	9.42	830.00	-1.28	1.6755	9.40

^a Taken from Ref. 15.^b Calculated with the method of Ref. 14.^c Calculated with Eqn (14).

Table 3. The I_p , $\Sigma SVEE_x$, ΔH_f^0 , and ΣPEI values of the monosubstituted alkanes RY

No.	RY ^a	$I_{p_{exp.}}$ (eV) ^b	$\Sigma SVEE_x$	ΔH_f^0 ^c	ΣPEI ^d	$I_{p_{calc.}}$ (eV) ^e
1	MeOH	10.84	221.60	-2.08	1.6243	10.91
2	EtOH	10.49	304.60	-2.43	1.7648	10.37
3	PrOH	10.10	387.60	-2.64	1.8130	10.17
4	i-PrOH	10.15	387.60	-2.83	1.9053	10.08
5	<i>n</i> -BuOH	10.04	470.60	-2.85	1.8365	10.06
6	<i>s</i> -BuOH		470.60	-3.03	1.9535	9.97
7	i-BuOH		470.60	-2.94	1.8611	10.04
8	OHC5		553.60	-3.05	1.8503	9.99
9	2OHC5		553.60	-3.22	1.9770	9.91
10	3OHC5		553.60	-3.26	2.0016	9.89
11	2m1OHC4		553.60	-3.12	1.8846	9.97
12	3m1OHC4		553.60	-3.12	1.8600	9.99
13	2m2OHC4		553.60	-3.41	2.0940	9.83
14	3m2OHC4		553.60	-3.25	2.0016	9.89
15	OHC6		636.60	-3.27	1.8593	9.95
16	2OHC6		636.60	-3.46	1.9908	9.87
17	OHC7		719.60	-3.49	1.8657	9.92
18	OHC8		802.60	-3.69	1.8704	9.89
19	2e1OHC6		802.60	-3.79	1.9309	9.86
20	OHC9		885.60	-3.90	1.8741	9.87
21	OHC10		968.60	-4.11	1.8770	9.86
22	OHC12		1134.60	-4.52	1.8814	9.83
23	OHC16		1466.60	-5.36	1.8868	9.80
24	MeOMe	9.98	304.60	-1.91	2.0000	10.04
25	EtOMe		387.60	-2.24	2.1405	9.82
26	PrOMe		470.60	-2.47	2.1887	9.76
27	i-PrOMe		470.60	-2.61	2.2810	9.69
28	<i>n</i> -BuOMe		553.60	-2.67	2.2122	9.74
29	<i>s</i> -BuOMe*		553.60	-2.83	2.3292	9.66
30	i-BuOMe*		553.60	-2.74	2.2368	9.72
31	<i>t</i> -BuOMe		553.60	-2.94	2.4215	9.60
32	C5OMe*		636.60	-2.90	2.2260	9.72
33	C6OMe*		719.60	-3.11	2.2350	9.72
34	C7OMe*		802.60	-3.33	2.2414	9.71
35	MeSH	9.44	192.20	-0.24	1.6243	9.55
36	EtSH	9.28	275.20	-0.48	1.7648	9.19
37	PrSH	9.19	358.20	-0.70	1.8130	9.15
38	i-PrSH		358.20	-0.79	1.9053	9.00
39	<i>n</i> -BuSH	9.14	441.20	-0.91	1.8365	9.17
40	<i>s</i> -BuSH		441.20	-1.00	1.9535	9.00
41	i-BuSH		441.20	-1.01	1.8611	9.13
42	<i>t</i> -BuSH		441.20	-1.14	2.0458	8.88
43	SHC5		524.20	-1.14	1.8503	9.19
44	2m2SHC4		524.20	-1.32	2.0940	8.90
45	3m1SHC4		524.20	-1.19	1.8600	9.17
46	3m2SHC4		524.20	-1.26	2.0016	9.01
47	SHC6		607.20	-1.35	1.8593	9.20
48	2m2SHC5		607.20	-1.54	2.1175	8.94
49	SHC7		690.20	-1.55	1.8657	9.22
50	SHC9		856.20	-1.98	1.8741	9.25
51	SHC10		939.20	-2.19	1.8770	9.26
52	MeSMe	8.69	275.20	-0.39	2.0000	8.66
53	EtSMe	8.55	358.20	-0.62	2.1405	8.59
54	PrSMe		441.20	-0.85	2.1887	8.67
55	i-PrSMe		441.20	-0.94	2.2810	8.54
56	<i>n</i> -BuSMe		524.20	-1.06	2.2122	8.76
57	<i>s</i> -BuSMe*		524.20	-1.16	1.3292	9.80
58	i-BuSMe*		524.20	-1.10	1.2368	9.91
59	<i>t</i> -BuSMe		524.20	-1.26	2.4215	8.51
60	<i>n</i> -C5SMe		607.20	-1.26	2.2260	8.83
61	C6SMe*		690.20	-1.48	2.2350	8.89
62	C7SMe*		773.20	-1.69	2.2414	8.94

(Continues)

Table 3. (Continued)

No.	RY ^a	$I_{p_{exp.}}$ (eV) ^b	$\Sigma SVEE_x$	ΔH_f^{0c}	ΣPEI^d	$I_{p_{calc.}}$ (eV)
63	MeNH ₂	8.97	207.90	-0.23	2.2486	9.02
64	EtNH ₂	8.86	290.90	-0.49	2.3891	8.82
65	PrNH ₂	8.78	373.90	-0.73	2.4373	8.75
66	i-PrNH ₂	8.72	373.90	-0.87	2.5296	8.72
67	n-BuNH ₂	8.71	456.90	-0.95	2.4608	8.72
68	i-BuNH ₂	8.70	456.90	-1.02	2.4854	8.71
69	s-BuNH ₂	8.70	456.90	-1.08	2.5778	8.68
70	t-BuNH ₂	8.64	456.90	-1.25	2.6701	8.66
71	MeBr	10.53	203.70	-0.37	1.0000	10.62
72	EtBr	10.29	286.70	-0.64	1.1405	10.24
73	PrBr	10.18	369.70	-0.90	1.1887	10.15
74	i-PrBr	10.075	369.70	-1.03	1.2810	10.04
75	n-BuBr	10.125	452.70	-1.11	1.2122	10.12
76	s-BuBr	9.98	452.70	-1.25	1.3292	10.00
77	t-BuBr	9.89	452.70	-1.37	1.4215	9.91
78	BrC5	10.10	535.70	-1.34	1.2260	10.10
79	BrC6		618.70	-1.54	1.2350	10.10
80	BrC7		701.70	-1.74	1.2414	10.09
81	BrC8		784.70	-1.96	1.2461	10.09
82	BrC12		1116.70	-2.80	1.2571	10.09
83	BrC16		1448.70	-3.63	1.2625	10.09
84	MeCl	11.30	210.60	-0.85	1.0000	11.34
85	EtCl	10.97	293.60	-1.16	1.1405	10.96
86	PrCl	10.82	376.60	-1.37	1.1887	10.78
87	i-PrCl	10.78	376.60	-1.50	1.2810	10.76
88	n-BuCl	10.67	459.60	-1.60	1.2122	10.67
89	s-BuCl	10.65	459.60	-1.67	1.3292	10.65
90	i-BuCl	10.66	459.60	-1.65	1.2368	10.67
91	t-BuCl	10.61	459.60	-1.89	1.4215	10.63
92	CiC5		542.60	-1.81	1.2260	10.60
93	3m1CiC4		542.60	-1.86	1.2357	10.60
94	3m2CiC4		542.60	-1.92	1.3773	10.57
95	2m2CiC4		542.60	-2.10	1.4932	10.55
96	2CiC6		625.60	-2.12	1.3665	10.53
97	CiC8		791.60	-2.48	1.2461	10.48
98	CiC12		1123.60	-3.33	1.2571	10.41
99	CiC18		1621.60	-4.62	1.2642	10.36
100	MeI	9.54	193.60	0.15	1.0000	9.59
101	EtI	9.33	276.60	-0.08	1.1405	9.30
102	PrI	9.26	359.60	-0.31	1.1887	9.26
103	i-PrI	9.17	359.60	-0.42	1.2810	9.14
104	t-BuI	9.02	442.60	-0.75	1.4215	9.04

^a m, methyl; e, ethyl, for example, 2m2SHC5 represents 2-methyl-2-butanethiol; The items marked with asterisk ^{***} indicate that the experimental heat of formation is unavailable for the compound, and its heat of formation was calculated with the method of Ref. ¹⁸.

^b Taken from Ref. ¹⁵.

^c Taken from Ref. ¹⁸.

^d Calculated with the method of Ref. ¹⁷.

^e Calculated with Eqns (15)–(20) in Table 4, respectively.

with the leave-one-out method and the obtained result (correlation coefficient $R_{cv} = 0.9996$ and standard error $Scv = 2.64$ eV) showed that the Eqn (14) has good stability and predictability.

Monosubstituted alkane RY

Generally, the first ionization of monosubstituted alkane RY (Y = OH, NH₂, SH, Cl, Br, and I) took place in the nonbonded electron pair on Y. In this case, the polarizability effect R_m of Eqn (11) should be displaced

with the sum of the Polarizability Effect Index (ΣPEI) of substituted groups attached to the Y.¹⁷ Using the I_p , $\Sigma SVEE_x$, ΔH_f^0 , and ΣPEI values of the homologs, ROH(R'), RNH₂, RSH(R'), RBr, RCl, and I (see Table 3), the correlation expressions (15)–(20) are obtained and are shown in Table 4.

All equations in Table 4 have good correlations. Using these equations to calculate the ionization potentials of the monosubstituted alkanes in Table 3, the average absolute error between the calculated and experimental values is only 0.035 eV. Furthermore, with Eqns (15)–(20) and the experimental heats of formation in Table 3, the

Table 4. The correlation expressions (15)–(20) for monosubstituted alkanes RY (Equation: $I_p \cdot N_{ve,m} = a + b[\sum SVEE_x - \Delta H_f^0] + c\Sigma PEI$)

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>R</i>	<i>S</i>	<i>n</i>	<i>F</i>	Equation
ROH(R')	38.8535 (± 14.6871)	0.6997 (± 0.0129)	-26.2629 (± 8.8083)	0.9996	2.2547	6	1754.97	15
RSH(R')	76.3407 (± 7.7798)	0.6771 (± 0.0096)	-44.86622 (± 4.5950)	0.9997	1.6864	6	2762.37	16
RNH ₂	19.2875 (± 7.5330)	0.6197 (± 0.0049)	-9.787679 (± 3.6543)	1.0000	0.6709	8	25339.19	17
RBr	32.2466 (± 4.1844)	0.7284 (± 0.0052)	-32.21111 (± 4.4222)	0.9999	1.0147	8	19033.81	18
RCI	10.5238 (± 3.1221)	0.7385 (± 0.0050)	-7.862444 (± 3.7101)	1.0000	0.6814	8	35293.86	19
RI	37.3872 (± 8.8082)	0.6788 (± 0.0209)	-34.43429 (± 12.6207)	0.9999	1.0201	5	6745.49	20

ionization potentials of some RY compounds are predicted and listed in Table 3, the reliability of the predicted results remains to be tested by further experiments.

DISCUSSION

The results of above-obtained Eqns (13)–(20) showed that Eqn (11) expresses the link between the ionization potential and the heat of formation for organic homologous compounds well. The coefficients before the term $(\sum SVEE_x - \Delta H_f^0)$ of Eqns (13)–(20) are all positive, and are in the range of 0.60–0.80, which indicates that the postulation of $I_p = a_0 E_{avm}$ is rational and the molecular average valence electronic energy E_{avm} is 1/0.60–1/0.8 (or 1.67–1.25) times of its first ionization potential. Therefore, Eqn (11) provides a new insight into the intercorrelation between the ionization potential and the heat of formation for organic homologous compounds.

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