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Enthalpies Estimation of Formation of Monosubstituted Alkanes by Interaction Potential Index

Ya-xin Wu^{a,b}, Chen-zhong Cao^{b*}, Hua Yuan^b*a. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China**b. School of Chemistry and Chemical Engineering, Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan University of Science and Technology, and Hunan Provincial University Key Laboratory of QSAR/QSPR, Xiangtan 411201, China*

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The interaction potential index IPI(X) of 16 kinds of substituents X (X=OH, SH, NH₂, Br, Cl, I, NO₂, CN, CHO, COOH, CH₃, CH=CH₂, C≡CH, Ph, COCH₃, COOCH₃) were proposed, which are derived from the experimental enthalpies of formation $\Delta_f H^\ominus(g)$ values of monosubstituted straight-chain alkanes. Based on the IPI(X) and polarizability effect index, a simple and effective model was constructed to estimate the $\Delta_f H^\ominus(g)$ values of monosubstituted alkanes RX (including the branched derivatives). The present model takes into account not only the contributions of the alkyl R and the substituent X, but also the contribution of the interaction between R and X. Its stability and prediction ability was confirmed by the results of leave-one-out method. Compared with previous reported studies, the obtained equation can be used to estimate enthalpies of formation for many more kinds of monosubstituted alkanes with fewer parameters. Thus, it is recommended for the calculation of the $\Delta_f H^\ominus(g)$ for the RX.

Key words: Interaction potential index, Substituent, Monosubstituted alkane, Enthalpy of formation, Polarizability effect index

I. INTRODUCTION

The enthalpy of formation is one of the most important thermodynamic parameters. However, the available experimental data of the enthalpies of formation $\Delta_f H^\ominus$ are relatively scarce and even not always reliable [1–3]. Thus the calculation of the $\Delta_f H^\ominus$ by theoretical method has attracted more and more attention [1–23]. Benson and co-workers contributed greatly to this field, and their additivity method has played an important role in estimating the $\Delta_f H^\ominus$ [4–6]. Actually, the accurate estimation, whether based on atom-centered groups additivity method or based on bond-centered groups additivity method, needs to calculate the contribution of each group or the different contribution values of a group in different chemical environment, respectively. Istomin and Palm ever divided the $\Delta_f H^\ominus$ of the monoderivatives of hydrocarbons $\Delta_f H^\ominus(RX)$ into three parts, and extended the additive rule to Eq.(1) [24–27],

$$\Delta_f H^\ominus(RX) = h[R] + h[X] + \varphi[R]\varphi[X] \quad (1)$$

where the $h[R]$ and $h[X]$ are the contributions of the alkyl R and the substituent X to the $\Delta_f H^\ominus(RX)$, respectively. The $\varphi[R]\varphi[X]$ represents the contribution of the interaction of R and X. It is considered that the $h[R]$ and $h[X]$ are easy to be calculated without considering the intramolecular mutual interaction. Thus, if the item $\varphi[R]\varphi[X]$ can be quantitatively described, the accurate $\Delta_f H^\ominus(RX)$ values will be obtained. However, this model was not further extended and applied, because the parameter φ defined empirically was not related to any known property of R or X [1–3, 28–30]. In our previous work, the product of the electronegativity χ of the radical atom of substituent X and the polarizability effect index (PEI) of the alkyl R is used to roughly scale the $\varphi[R]\varphi[X]$. It is noted that the electronegativity of the radical atom can not distinguish those substituents, whose radical atom is the same, such as –CHO and –COOH, or –NH₂ and –NO₂. However, it is commonly believed that the structural characteristic and their influence on the molecular properties of these groups are different. Thus, a further investigation is needed to determine how much their contributions are.

In this work, the interaction potential index IPI(X) were proposed for the X groups of OH, SH, NH₂, Br, Cl, I, NO₂, CN, CHO, COOH, CH₃, CH=CH₂, C≡CH, Ph, COCH₃, and COOCH₃. Subsequently, a simple

* Author to whom correspondence should be addressed. E-mail: czcao@hnust.edu.cn

TABLE I Regression results of Eq.(5) for each series of $H(CH_2)_nX_i$.

Series	$H(CH_2)_nX_i$	n	$h[X_i]$	$h[CH_2]_i$	$IPI(X_i)$	r^*	$s^*/(kJ/mol)$
1	$H(CH_2)_nOH$	12	-118.7746	-19.7857	-63.8984	0.9999	1.53
2	$H(CH_2)_nSH$	9	20.0051	-20.3205	-22.5082	1.0000	0.45
3	$H(CH_2)_nNH_2$	4	25.8477	-21.2228	-27.1200	1.0000	0.05
4	$H(CH_2)_nBr$	10	41.4442	-20.0079	-56.6000	1.0000	0.84
5	$H(CH_2)_nCl$	8	-14.7096	-20.6222	-47.2530	1.0000	1.22
6	$H(CH_2)_nI$	3	42.4872	-21.5867	-6.5005	1.0000	0.00
7	$H(CH_2)_nNO_2$	4	12.0788	-18.3722	-68.0172	1.0000	0.12
8	$H(CH_2)_nCN$	8	94.1184	-20.6899	0.0000	0.9999	0.99
9	$H(CH_2)_nCHO$	9	-144.4194	-20.6317	0.0000	0.9995	2.00
10	$H(CH_2)_nCOOH$	11	-412.0789	-20.5433	0.0000	0.9996	2.39
11	$H(CH_2)_nCH_3$	13	-63.3127	-20.6902	0.0000	1.0000	0.75
12	$H(CH_2)_nCH=CH_2$	9	40.8464	-20.6192	0.0000	0.9999	1.02
13	$H(CH_2)_nC\equiv CH$	3	205.7355	-20.4806	0.0000	1.0000	0.56
14	$H(CH_2)_nPh$	5	71.6440	-21.0160	0.0000	1.0000	0.57
15	$H(CH_2)_nCOCH_3$	5	-196.9717	-20.5377	0.0000	1.0000	0.40
16	$H(CH_2)_nCOOCH_3$	12	-390.8942	-20.4417	0.0000	0.9998	1.57

* r : correlation coefficient; s : standard error.

and effective model based on Eq.(1) was developed, and used to estimate the $\Delta_f H^\circ(g)$ for the RX (including the branched derivatives).

II. COMPUTATIONAL METHOD

For the homologous series of monosubstituted straight-chain alkanes $H(CH_2)_nX$ ($n=1, 2, 3, \dots$), the contributions of steric effects to their enthalpies of formation are very small and can be neglected. Thus, the item $\varphi[R]$ in Eq.(1) can be scaled by the polarizability effect index of the alkyl PEI(R) [28–32]. The item $h[R]$ in Eq.(1) of a homologous series can be expressed by [5, 33, 34],

$$h[R] = N_C h[CH_2] \quad (2)$$

N_C is the number of C atom of the alkyl R. $h[CH_2]$ is the contribution of each CH_2 group to the $\Delta_f H^\circ$. From the above analysis, we can lead to Eq.(3) for the $\Delta_f H^\circ$ of $H(CH_2)_nX$,

$$\Delta_f H^\circ(H(CH_2)_nX) = h[X] + N_C h[CH_2] + gPEI(R)\varphi[X] \quad (3)$$

g is a constant, and the item $g\varphi[X]$ is used to scale the interaction potential of the X with an alkyl, which is defined as the interaction potential index IPI(X) in this work. Thus Eq.(3) can be modified as Eq.(4).

$$\Delta_f H^\circ(H(CH_2)_nX) = h[X] + N_C h[CH_2] + IPI(X)PEI(R) \quad (4)$$

For a given series $H(CH_2)_nX_i$, the parameters $h[X_i]$, $h[CH_2]_i$, and $IPI(X_i)$ are constants. Therefore, the

$\Delta_f H^\circ(H(CH_2)_nX_i)$ can be correlated only with N_C and $PEI(R)$, as shown in Eq.(5).

$$\Delta_f H^\circ(H(CH_2)_nX_i) = h[X_i] + h[CH_2]N_C + IPI(X_i)PEI(R) \quad (5)$$

Take the experimental enthalpies of formation $\Delta_f H^\circ(g)_{exp.}$ of each series $H(CH_2)_nX_i$ ($X_i=OH, SH, NH_2, Br, Cl, I, NO_2, CN, CHO, COOH, CH_3, CH=CH_2, C\equiv CH, Ph, COCH_3, COOCH_3$) as data sets, to correlate with parameters N_C and $PEI(R)$, we got coefficients $h[CH_2]_i$, $IPI(X_i)$ and $h[X_i]$ of these 16 series. The regression results and data were given in Tables I and II.

In Table I, all the values of correlation coefficients r exceed 0.9995. The average absolute error between the experimental values and the calculated values in Table II is only 0.8 kJ/mol. It indicated that the Eq.(5) is effective to estimate the $\Delta_f H^\circ(g)$ for $H(CH_2)_nX$. From Table I, it can also be seen that the $h[CH_2]_i$ values of 16 series, fluctuates within a very small range (from -18.4 to -21.6). Their average value is -20.5, which is closed to the $h[CH_2]$ value of the series $H(CH_2)_nCH_3$ (-20.69). It is well known that there is no polar group in the straight-chain alkane molecule, so the group contribution of each CH_2 can be taken as a constant. This result indicated that after removing the effects of the intramolecular mutual interaction, the $h[CH_2]$ of different series is approximately equal to that of the straight-chain alkane series. It should be noted that the numbers of samples of some series, such as $H(CH_2)_3I$ and $H(CH_2)_3C\equiv CH$, are less than 6, and their r values reach 1.0000 (see Table I). In general, the more samples in regression, the more reliability in fitting procedure. How-

TABLE II The $\Delta_f H^\circ$ (g) (kJ/mol), N_C , and PEI(R) values for $H(CH_2)_n X_i$.

$H(CH_2)_n X_i$	No.	Compounds	$\Delta_f H^\circ$ (g) _{exp.}	N_C	PEI(R)	$\Delta_f H^\circ$ (g) _{calc.} ^a	Δ ^b
H(CH ₂) _n OH	1	MeOH	-201.0	1	1.0000	-202.5	1.5
	2	EtOH	-234.8	2	1.1405	-231.2	-3.6
	3	PrOH	-255.1	3	1.1887	-254.1	-1.0
	4	<i>n</i> -BuOH	-274.6	4	1.2122	-275.4	0.8
	5	H(CH ₂) ₅ OH	-294.6	5	1.2260	-296.0	1.4
	6	H(CH ₂) ₆ OH	-315.9	6	1.2350	-316.4	0.5
	7	H(CH ₂) ₇ OH	-336.5	7	1.2414	-336.6	0.1
	8	H(CH ₂) ₈ OH	-355.6	8	1.2461	-356.7	1.1
	9	H(CH ₂) ₉ OH	-376.5	9	1.2498	-376.7	0.2
	10	H(CH ₂) ₁₀ OH	-396.6	10	1.2527	-396.7	0.1
	11	H(CH ₂) ₁₂ OH	-436.6	12	1.2571	-436.5	-0.1
	12	H(CH ₂) ₁₆ OH	-517.0	16	1.2625	-516.0	-1.0
H(CH ₂) _n SH	1	MeSH	-22.9	1	1.0000	-22.8	-0.1
	2	EtSH	-46.1	2	1.1405	-46.3	0.2
	3	PrSH	-67.8	3	1.1887	-67.7	-0.1
	4	<i>n</i> -BuSH	-88.0	4	1.2122	-88.6	0.6
	5	H(CH ₂) ₅ SH	-110.0	5	1.2260	-109.2	-0.8
	6	H(CH ₂) ₆ SH	-129.9	6	1.2350	-129.7	-0.2
	7	H(CH ₂) ₇ SH	-149.9	7	1.2414	-150.2	0.3
	8	H(CH ₂) ₉ SH	-190.8	9	1.2498	-191.0	0.2
	9	H(CH ₂) ₁₀ SH	-211.5	10	1.2527	-211.4	-0.1
CH ₃ (CH ₂) _n NH ₂	1	MeNH ₂	-22.5	1	1.0000	-22.5	0.0
	2	EtNH ₂	-47.5	2	1.1405	-47.5	0.0
	3	PrNH ₂	-70.1	3	1.1887	-70.1	0.0
	4	<i>n</i> -BuNH ₂	-91.9	4	1.2122	-91.9	0.0
H(CH ₂) _n Br	1	MeBr	-35.4	1	1.0000	-35.2	-0.2
	2	EtBr	-61.9	2	1.1405	-63.1	1.2
	3	PrBr	-87.0	3	1.1887	-85.9	-1.1
	4	<i>n</i> -BuBr	-107.1	4	1.2122	-107.2	0.1
	5	H(CH ₂) ₅ Br	-128.9	5	1.2260	-128.0	-0.9
	6	H(CH ₂) ₆ Br	-148.3	6	1.2350	-148.5	0.2
	7	H(CH ₂) ₇ Br	-167.8	7	1.2414	-168.9	1.1
	8	H(CH ₂) ₈ Br	-189.3	8	1.2461	-189.1	-0.2
	9	H(CH ₂) ₁₂ Br	-269.9	12	1.2571	-269.8	-0.1
	10	H(CH ₂) ₁₆ Br	-350.2	16	1.2625	-350.1	-0.1
H(CH ₂) _n Cl	1	MeCl	-81.9	1	1.0000	-82.6	0.7
	2	EtCl	-112.1	2	1.1405	-109.8	-2.3
	3	PrCl	-131.9	3	1.1887	-132.7	0.8
	4	<i>n</i> -BuCl	-154.4	4	1.2122	-154.5	0.1
	5	H(CH ₂) ₅ Cl	-174.9	5	1.2260	-175.8	0.9
	6	H(CH ₂) ₈ Cl	-238.9	8	1.2461	-238.6	-0.3
	7	H(CH ₂) ₁₂ Cl	-321.1	12	1.2571	-321.6	0.5
	8	H(CH ₂) ₁₈ Cl	-446.0	18	1.2642	-445.6	-0.4
H(CH ₂) _n I	1	MeI	14.4	1	1.0000	14.4	0.0
	2	EtI	-8.1	2	1.1405	-8.1	0.0
	3	PrI	-30.0	3	1.1887	-30.0	0.0
H(CH ₂) _n NO ₂	1	MeNO ₂	-74.3	1	1.0000	-74.3	0.0
	2	EtNO ₂	-102.3	2	1.1405	-102.2	-0.1

To be continued.

Table II continued.

$H(CH_2)_nX_i$	No.	Compounds	$\Delta_f H^\ominus(g)_{\text{exp.}}$	N_C	PEI(R)	$\Delta_f H^\ominus(g)_{\text{calc.}}^a$	Δ^b	
$H(CH_2)_nNO_2$	3	PrNO ₂	-123.8	3	1.1887	-123.9	0.1	
	4	<i>n</i> -BuNO ₂	-143.9	4	1.2122	-143.9	0.0	
	$H(CH_2)_nCN$	1	MeCN	74.0	1	1.0000	73.4	0.6
		2	EtCN	51.7	2	1.1405	52.7	-1.0
3		PrCN	33.6	3	1.1887	32.0	1.6	
4		<i>n</i> -BuCN	10.5	4	1.2122	11.4	-0.9	
5		H(CH ₂) ₆ CN	-31.0	6	1.2350	-30.0	-1.0	
6		H(CH ₂) ₇ CN	-50.5	7	1.2414	-50.7	0.2	
7		H(CH ₂) ₉ CN	-91.5	9	1.2498	-92.1	0.6	
$H(CH_2)_nCHO$	8	H(CH ₂) ₁₃ CN	-174.9	13	1.2587	-174.9	0.0	
	1	MeCHO	-166.2	1	1.0000	-165.1	-1.1	
	2	EtCHO	-185.6	2	1.1405	-185.7	0.1	
	3	PrCHO	-204.8	3	1.1887	-206.3	1.5	
	4	<i>n</i> -BuCHO	-228.4	4	1.2122	-226.9	-1.5	
	5	H(CH ₂) ₅ CHO	-248.6	5	1.2260	-247.6	-1.0	
	6	H(CH ₂) ₆ CHO	-263.8	6	1.2350	-268.2	4.4	
	7	H(CH ₂) ₇ CHO	-289.6	7	1.2414	-288.8	-0.8	
$H(CH_2)_nCOOH$	8	H(CH ₂) ₈ CHO	-310.3	8	1.2461	-309.5	-0.8	
	9	H(CH ₂) ₉ CHO	-330.9	9	1.2498	-330.1	-0.8	
	1	MeCOOH	-432.2	1	1.0000	-432.6	0.4	
	2	EtCOOH	-455.7	2	1.1405	-453.2	-2.5	
	3	PrCOOH	-475.9	3	1.1887	-473.7	-2.2	
	4	<i>n</i> -BuCOOH	-491.9	4	1.2122	-494.3	2.4	
	5	H(CH ₂) ₅ COOH	-511.9	5	1.2260	-514.8	2.9	
	6	H(CH ₂) ₆ COOH	-536.2	6	1.2350	-535.3	-0.9	
	7	H(CH ₂) ₇ COOH	-554.3	7	1.2414	-555.9	1.6	
	8	H(CH ₂) ₈ COOH	-577.3	8	1.2461	-576.4	-0.9	
	9	H(CH ₂) ₉ COOH	-594.5	9	1.2498	-597.0	2.5	
$H(CH_2)_nCH_3$	10	H(CH ₂) ₁₁ COOH	-642.0	11	1.2551	-638.1	-3.9	
	11	H(CH ₂) ₁₄ COOH	-699.0	14	1.2602	-699.7	0.7	
	1	MeCH ₃	-84.0	1	1.0000	-84.0	0.0	
	2	EtCH ₃	-103.8	2	1.1405	-104.7	0.9	
	3	PrCH ₃	-125.7	3	1.1887	-125.4	-0.3	
	4	<i>n</i> -BuCH ₃	-146.9	4	1.2122	-146.1	-0.8	
	5	H(CH ₂) ₅ CH ₃	-166.9	5	1.2260	-166.8	-0.1	
	6	H(CH ₂) ₆ CH ₃	-187.6	6	1.2350	-187.5	-0.1	
	7	H(CH ₂) ₇ CH ₃	-208.5	7	1.2414	-208.1	-0.4	
	8	H(CH ₂) ₈ CH ₃	-228.2	8	1.2461	-228.8	0.6	
	9	H(CH ₂) ₉ CH ₃	-249.5	9	1.2498	-249.5	0.0	
	10	H(CH ₂) ₁₀ CH ₃	-270.8	10	1.2527	-270.2	-0.6	
	11	H(CH ₂) ₁₁ CH ₃	-289.4	11	1.2551	-290.9	1.5	
12	H(CH ₂) ₁₅ CH ₃	-374.8	15	1.2614	-373.7	-1.1		
$H(CH_2)_nCH=CH_2$	13	H(CH ₂) ₁₇ CH ₃	-414.6	17	1.2634	-415.0	0.4	
	1	MeCH=CH ₂	20.0	1	1.0000	20.2	-0.2	
	2	EtCH=CH ₂	0.1	2	1.1405	-0.4	0.5	
	3	PrCH=CH ₂	-21.1	3	1.1887	-21.0	-0.1	
	4	<i>n</i> -BuCH=CH ₂	-43.5	4	1.2122	-41.6	-1.9	
5	H(CH ₂) ₅ CH=CH ₂	-62.3	5	1.2260	-62.2	-0.1		

To be continued.

Table II continued.

$H(CH_2)_nX_i$	No.	Compounds	$\Delta_f H^\ominus(g)_{\text{exp.}}$	N_C	PEI(R)	$\Delta_f H^\ominus(g)_{\text{calc.}}$ ^a	Δ^b
	6	$H(CH_2)_6CH=CH_2$	-81.3	6	1.2350	-82.9	1.6
	7	$H(CH_2)_8CH=CH_2$	-123.3	8	1.2461	-124.1	0.8
	8	$H(CH_2)_{10}CH=CH_2$	-165.4	10	1.2527	-165.3	-0.1
	9	$H(CH_2)_{14}CH=CH_2$	-248.4	14	1.2602	-247.8	-0.6
$H(CH_2)_nC\equiv CH$	1	MeC \equiv CH	184.9	1	1.0000	185.3	-0.4
	2	EtC \equiv CH	165.2	2	1.1405	164.8	0.4
	3	$H(CH_2)_7C\equiv CH$	62.3	7	1.2414	62.4	-0.1
$H(CH_2)_nPh$	1	MePh	50.5	1	1.0000	50.6	-0.1
	2	EtPh	29.9	2	1.1405	29.6	0.3
	3	PrPh	7.9	3	1.1887	8.6	-0.7
	4	<i>n</i> -BuPh	-11.8	4	1.2122	-12.4	0.6
	5	$H(CH_2)_{10}Ph$	-138.6	10	1.2527	-138.5	-0.1
$H(CH_2)_nCOCH_3$	1	MeCOCH ₃	-217.1	1	1.0000	-217.5	0.4
	2	EtCOCH ₃	-238.5	2	1.1405	-238.0	-0.5
	3	PrCOCH ₃	-258.8	3	1.1887	-258.6	-0.2
	4	<i>n</i> -BuCOCH ₃	-278.9	4	1.2122	-279.1	0.2
	5	$H(CH_2)_7COCH_3$	-340.7	7	1.2414	-340.7	0.0
$H(CH_2)_nCOOCH_3$	1	MeCOOCH ₃	-413.3	1	1.0000	-411.3	-2.0
	2	<i>n</i> -BuCOOCH ₃	-471.1	4	1.2122	-472.7	1.6
	3	$H(CH_2)_5COOCH_3$	-492.2	5	1.2260	-493.1	0.9
	4	$H(CH_2)_6COOCH_3$	-515.5	6	1.2350	-513.5	-2.0
	5	$H(CH_2)_7COOCH_3$	-533.9	7	1.2414	-534.0	0.1
	6	$H(CH_2)_8COOCH_3$	-554.2	8	1.2461	-554.4	0.2
	7	$H(CH_2)_9COOCH_3$	-573.8	9	1.2498	-574.9	1.1
	8	$H(CH_2)_{10}COOCH_3$	-593.8	10	1.2527	-595.3	1.5
	9	$H(CH_2)_{11}COOCH_3$	-614.9	11	1.2551	-615.8	0.9
	10	$H(CH_2)_{12}COOCH_3$	-635.3	12	1.2571	-636.2	0.9
	11	$H(CH_2)_{13}COOCH_3$	-656.9	13	1.2587	-656.6	-0.3
	12	$H(CH_2)_{14}COOCH_3$	-680.0	14	1.2602	-677.1	-2.9

In this table, unless otherwise stated, the experimental enthalpies of formation are taken from Refs. [30], [35].

^a Calculated by Eq.(5).

^b $\Delta = \Delta_f H^\ominus_{\text{exp.}} - \Delta_f H^\ominus_{\text{calc.}}$.

ever, for lack of experimental data of the enthalpies of formation, the number of samples of these series is less than 6. Fortunately, the most important purpose of the regression analysis according to Eq.(5) is to obtain the parameters IPI(X_i) and $h[X_i]$, but not to get a better regression result. So, the number of samples (3–5) can be competent.

We noted that the IPI(X) values are zero (see Table I) for those substituents with C atom as the radical atom, such as CH₃ and CHO. It means that the $\Delta_f H^\ominus(g)_{\text{exp.}}$ values have good correlation only with N_C for those series, and the last item in Eq.(5) can be neglected in regression. On the other hand, with respect to groups NH₂ and NO₂, although both of their radical atoms are N atoms, their IPI(X) values are far from each other. From the above results, we can draw out a conclusion: if the radical atom of the X is carbon

atom, the $\Delta_f H^\ominus(H(CH_2)_nX)$ in Eq.(4) can be well estimated only with the $h[X]$ and $N_C h[CH_2]$ without the last item IPI(X)PEI(R). Otherwise the contributions of the $\varphi[R]\varphi[X]$ to the $\Delta_f H^\ominus(H(CH_2)_nX)$ can not be neglected. Why? The interaction between an alkyl R and the substituent X is considered to be closely related to the properties of the C–X bond. For the X group with C atom as the radical atom, there is a non-polar C–C bond between the R and X. So their interaction is very small, and can be neglected. In Ref.[1], it is considered that the interaction of substituents with an alkyl group is controlled mainly by the radical atom of the substituents. The results of Table I show that the statement of Ref.[1] is incomplete for substituents with no-carbon atom as the radical atom.

Based on above results, Eq.(4) can be modified as Eq.(6) to express the $\Delta_f H^\ominus$ for various series of mono-

TABLE III The IPI(X), χ of the radical atom, and χ_G values for substituents X.

X	χ_P	χ_{AR}	χ_S	$\chi_{G-Sanderson}$	$\chi_{G-Bratsch}$	χ_{G-Ve}	IPI(X)
OH	3.44	3.50	3.654	3.078	2.684	3.263	-63.8984
SH	2.58	2.44	2.954	2.767	2.375	2.526	-22.5082
NH ₂	3.04	3.07	3.194	2.779	2.423	2.800	-27.1200
Br	2.96	2.74	3.219	3.219	2.96	2.96	-56.6000
Cl	3.16	2.83	3.475	3.475	3.16	3.16	-47.2530
I	2.66	2.21	2.778	2.778	2.66	2.66	-6.5005
NO ₂	3.04	3.07	3.194	3.494	3.295	3.322	-68.0172
CN	2.55	2.5	2.746	2.962	2.774	2.822	0.0000
CHO	2.55	2.5	2.746	2.963	2.638	3.004	0.0000
COOH	2.55	2.5	2.746	3.122	2.801	3.158	0.0000
CH ₃	2.55	2.5	2.746	2.630	2.278	2.400	0.0000
CH=CH ₂	2.55	2.5	2.746	2.653	2.328	2.455	0.0000
C≡CH	2.55	2.5	2.746	2.694	2.422	2.511	0.0000
Ph	2.55	2.5	2.746	2.675	2.378	2.490	0.0000
COCH ₃	2.55	2.5	2.746	2.798	2.460	2.802	0.0000
COOCH ₃	2.55	2.5	2.746	2.907	2.565	2.969	0.0000

χ_P , χ_{AR} , and χ_S are the electronegativity in the scales of Pauling, Allred-Rochow, and Sanderson, respectively.

$\chi_{G-Sanderson}$, $\chi_{G-Bratsch}$, and χ_{G-Ve} are the group electronegativity calculated by Sanderson method, Bratsch method, and valence electrons equilibration method, respectively.

substituted straight-chain alkanes.

$$\Delta_f H^\ominus(\text{H}(\text{CH}_2)_n\text{X}) - h[\text{X}] = dN_C + e\text{IPI}(\text{X})\text{PEI}(\text{R}) \quad (6)$$

d and e are coefficients.

III. RESULTS AND DISCUSSION

A. Comparison with the reported electronegativity

Exner and Böhm proposed that the electronegativity of a group X can be expressed by the electronegativity χ of its radical atom (for example, the electronegativity of OH group is expressed by that of O atom, 3.44) [1]. Our group also used the χ of the radical atom of a group X to express the interaction potential of the X with alkyl groups [28–30]. The IPI(X) was correlated with the χ of the radical atom of X in the scales of Pauling [36], Allred-Rochow [37], and Sanderson [38], respectively (see Table III). The best correlation is $r=0.9150$ (with Sanderson scale). Its dependence is shown in Fig.1. Subsequently, we searched for the correlation of IPI(X) to the group electronegativity calculated by Sanderson method [39], Bratsch method [40], and valence electrons equilibration method [41], respectively. We get even worse relations ($r<0.75$). That is to say the parameter IPI(X) of a group is not the same as the electronegativity of its radical atom or its group electronegativity, but a new scale.

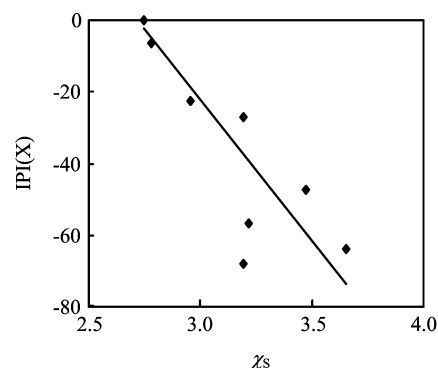


FIG. 1 The χ (with Sanderson scale) of the radical atom of substituents X *vs.* IPI(X). $\text{IPI}(\text{X})=213.76-78.67\chi_s$, $r=0.9150$.

B. Predicting the enthalpies of formation of RX

To test the efficiency of the interaction potential index IPI(X), we employed it to estimate the $\Delta_f H^\ominus(\text{g})$ for monosubstituted alkanes RX (including the branched derivatives). With respect to branched derivatives, the contribution of an alkyl R to the $\Delta_f H^\ominus(\text{RX})$ is different from that of the monosubstituted straight-chain alkanes. Hence, one more parameter $\Delta\text{PEI}(\text{R})$ (the increment of PEI(R) of the branched alkyl to that of the straight-chain alkyl with the same carbon atom number, see Eq.(7)) was used to scale the contributions of the alkyl R to the enthalpies of formation, and Eq.(6) was modified as Eq.(9) to express the $\Delta_f H^\ominus(\text{g})$ for RX.

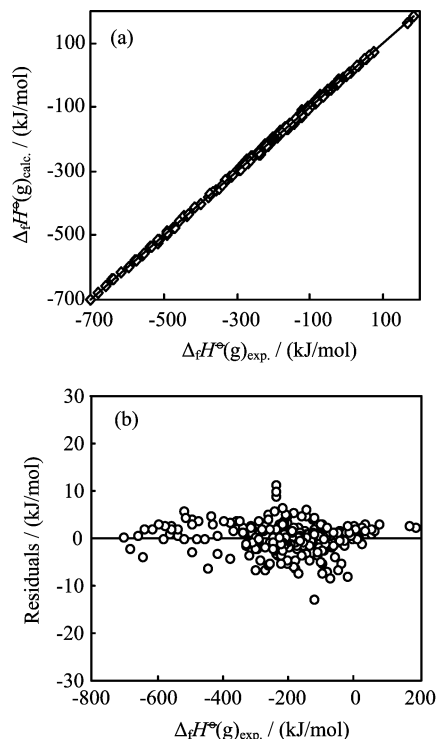


FIG. 2 Plots of $\Delta_f H^\ominus(\text{g})_{\text{calc.}}$ and residuals calculated with Eq.(10) vs. $\Delta_f H^\ominus(\text{g})_{\text{exp.}}$.

It deserves attention that there is $\Delta\text{PEI}(\text{R})=0$ for the monosubstituted straight-chain alkanes.

$$\Delta\text{PEI}(\text{R}) = \text{PEI}(\text{R})_{\text{branched}} - \text{PEI}(\text{R})_{\text{straight-chain}} \quad (7)$$

For example, the calculation of $\Delta\text{PEI}(\text{R})$ of *i*-Bu is as follows,

$$\begin{aligned} \Delta\text{PEI}(i\text{-Bu}) &= \text{PEI}(i\text{-Bu}) - \text{PEI}(n\text{-Bu}) \\ &= 1.2368 - 1.2122 = 0.0246 \end{aligned} \quad (8)$$

$$\Delta_f H^\ominus(\text{RX}) - h[\text{X}] = aN_{\text{C}} + b\text{IPI}(\text{X})\text{PEI}(\text{R}) + c\Delta\text{PEI}(\text{R}) \quad (9)$$

a, *b*, and *c* are coefficients.

Taking the experimental enthalpies of formation values $\Delta_f H^\ominus(\text{g})_{\text{exp.}}$ of 220 monosubstituted alkanes as a data set, we make a regression analysis with N_{C} , $\text{IPI}(\text{X})\text{PEI}(\text{R})$ and $\Delta\text{PEI}(\text{R})$, and obtain

$$\Delta_f H^\ominus(\text{RX}) - h[\text{X}] = -20.5682N_{\text{C}} + 0.9607\text{IPI}(\text{X}) \cdot \text{PEI}(\text{R}) - 68.5445\Delta\text{PEI}(\text{R}) \quad (10)$$

$$r = 0.9989, \quad s = 3.51 \text{ kJ/mol}, \quad n = 220,$$

$$F = 149914.82, \quad r_{\text{cv}} = 0.9998, \quad s_{\text{cv}} = 3.38 \text{ kJ/mol}$$

Eq.(10) has a good correlation. The *a* and *b* of Fig.2 are the plots of $\Delta_f H^\ominus(\text{g})_{\text{calc.}}$ and residuals calculated with Eq.(10) vs. $\Delta_f H^\ominus(\text{g})_{\text{exp.}}$, respectively. The average absolute error between the experimental values and the calculated values is only 2.5 kJ/mol, within the experimental uncertainties (the experimental and calculated

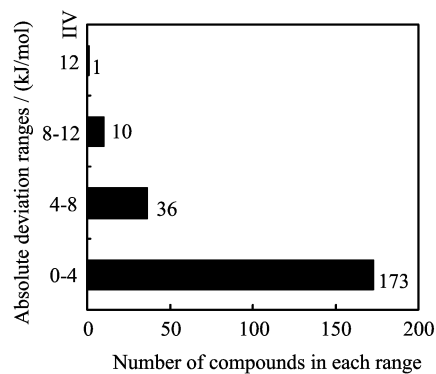


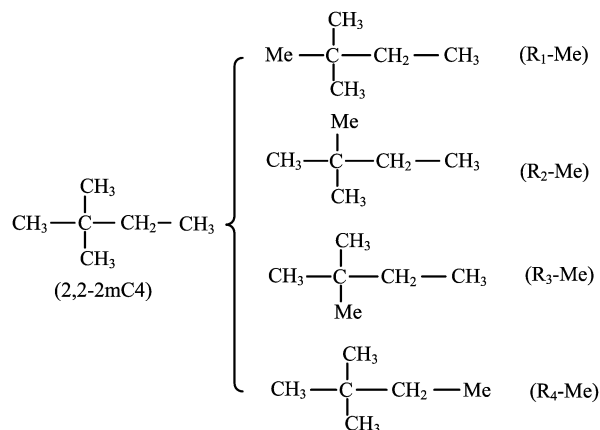
FIG. 3 Absolute deviation ranges of the experimental and the calculated values.

values are listed in the Supplementary material). The absolute deviation ranges of the experimental and the calculated values are reported in Fig.3. It can be observed that the numbers of absolute error in the range of 0–4, 4–8, 8–12, and ≥ 12 kJ/mol are 173, 36, 10, and 1, accounting for 78.6%, 16.4%, 4.5%, and 0.5%, respectively.

It should be noted that three or more $-\text{CH}_3$ can be taken as substituents for the calculation of $\text{PEI}(\text{R})$ in branched-chain alkanes. So the $\text{PEI}(\text{R})$ of branched-chain alkanes should be calculated by Eq.(11).

$$\text{PEI}(\text{R}) = \left[\prod_{i=1}^n \text{PEI}(\text{R})_i \right]^{1/n} \quad (11)$$

where $\text{PEI}(\text{R})_i$ is the polarizability effect index of a particular alkyl *i*. For example, the calculation of $\text{PEI}(\text{R})$ for 2,2-dimethyl butane (2,2-2mC4),



$$\begin{aligned} \text{PEI}(\text{R})_{2,2\text{-}2\text{mC}_4} &= (\text{PEI}(\text{R}_1)\text{PEI}(\text{R}_2)\text{PEI}(\text{R}_3)\text{PEI}(\text{R}_4))^{1/4} \\ &= (1.4697 \times 1.4697 \times 1.4697 \times 1.2849)^{1/4} = 1.4211. \end{aligned}$$

Compared with previous studies [28, 30], we successfully estimated enthalpies of formation for much more kinds of compounds with less parameters. Thus, it is indicated that the $\text{IPI}(\text{X})$ is effective in estimating

the enthalpies of formation of monosubstituted alkanes. In addition, the Eq.(10) is employed to predict the $\Delta_f H^\ominus(g)$ for over 2000 monosubstituted alkanes, and these predicted values are given in the Supplementary material.

IV. CONCLUSION

The interaction potential index IPI(X) has a specific physical meaning, and shows a good performance in estimating the contribution of the interaction potential of substituents with an alkyl group to the enthalpies of formation. The Eq.(10) takes into account not only the contributions of the alkyl R and the substituent X, but also the contribution of the interaction between R and X. In the present method, only parameters $h[X]$ and IPI(X) come from experimental values. It is simpler and more rapid than the Benson's additivity method, and Eq.(10) is recommended for the calculation of the $\Delta_f H^\ominus(g)$ for monosubstituted alkanes RX. With Eq.(10), over 2000 enthalpies of formation values of the RX were predicted.

Supplementary material: The predicted enthalpies of values of enthalpies of formation and related parameters of over 2000 monosubstituted alkanes are given.

V. ACKNOWLEDGMENTS

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