

## On Molecular Polarizability. 4. Evaluation of the Ionization Potential for Alkanes and Alkenes with Polarizability

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To express the influence of polarizability effect on ionization potential (Ip), the Geometric Mean Polarizability Effect Index (GMPEI) and Geometric Mean Polarizability Effect Index of  $\pi$  Bond (GMPEI $\pi$ ) were proposed for alkanes and alkenes, respectively. Taking a few of the compounds as a model, we obtained the correlation equations between the experimental Ip and GMPEI or GMPEI $\pi$  and then, with the obtained equations, we evaluated the Ip for the title compounds. The estimated Ip values by this work are in good agreement with the measured ones. Furthermore, the ab initio (#HF/6-31G\*\* OPT, Gaussian 98 program) and semiempirical (AM1) Ip computation are finished, and other topological index correlations with the Ip of alkane are discussed.

### 1. INTRODUCTION

Molecular polarizability is an important property related to electron movements. Many papers have investigated the effective polarizability effects on the organic compound properties in gas phase (such as protonic acidities and basicities)<sup>1–5</sup> and the X-ray photoelectron spectroscopy.<sup>6–8</sup> Previous works showed that the molecular polarizability is an important factor affecting organic compound properties related to positive or negative charge. Recently, an author proposed a formula to quantify the polarizability effect of alkyl substituents<sup>9</sup> and set up a general approach for evaluating the ionization potential of the monosubstituted paraffins.<sup>10</sup> However, this method is limited in application of alkanes and alkenes because their molecular structures are different from that of monosubstituted paraffins. As we know, the molecular ionization is corresponding to the ejection of an electron from the highest occupied molecular orbital (HOMO). For the monosubstituted paraffins, its electron is ejected from the nonbonding orbital or the  $\pi$  orbital of functional group. So the influence of substituent polarizability effect on its ionization is easily calculated. While alkane does not have a specific functional group and alkene has a nonpolar functional group, C=C, in which either atom can connect with alkyl groups; therefore, unlike it did in the monosubstituted paraffins, it is difficult to determine how the substituent polarizability effect comes into play in their ionization process. In principle, the ionization potential of alkanes and alkenes can be calculated by means of quantum chemistry. But in fact, there is still a larger error between the experimental and calculated ionization potential values, as seen in the next section of this paper. Joantéguy et al.<sup>11</sup> has pointed out that Ip cannot be calculated with an accuracy of 0.1 eV through quantum mechanical calculations, either at the semiempirical level (e.g. AM1), or DFT level, for reasons related to both methods and geometry accuracy. If a functional is accurate for  $\pi$  molecules as C<sub>2</sub>H<sub>4</sub>, any substitution by  $\sigma$  groups should deteriorate the performance.<sup>11</sup>

So this work tries to develop a nonquantum method for the evaluations of ionization potentials of alkanes and alkenes.

### 2. MODELING FOR THE IONIZATION POTENTIAL OF ALKANES AND ALKENES

**Ionization Potential of Alkanes.** According to the definitions that electronegativity of any chemical species (an atom or a molecule) is the negative of its chemical potential, the ionization potential of alkanes should mainly depend on its molecular electronegativity. But it should be noted that their molecular electronegativities vary only from 2.262 of methane (CH<sub>4</sub>) to 2.298 of decane (C<sub>10</sub>H<sub>22</sub>) (approximate to 2.3) in accordance with Bratsch's electronegativity equalization method<sup>12</sup> (Harmonic mean, with Pauling electronegativity units); however, their first ionization potentials drop from 12.61 down to 9.65 eV (decrease about 3.0 eV) correspondingly. It implies that the difference among alkane molecular ionization potentials does not originate from their molecular electronegativity and may result from other important factors. The dominant factor affecting this difference perhaps, we think, is the molecular polarizability of alkanes. It is known that the molecular ionization process is followed by a more or less strong electronic relaxation, which related to the polarizability. The substituent polarizability also is named as "the final-state effect"<sup>6</sup> and has a fundamental influence on chemical reactivity especially in the gas phase.<sup>7</sup> Suppose each carbon atom (or unit CH<sub>3</sub>, –CH<sub>2</sub>, >CH and >C<) bears fractional positive charge after ejection of an electron from the gas-phase alkane molecule, that is, the rearrangement, or relaxation, of the charge distribution upon the whole molecule, the charged alkane molecule [C<sub>n</sub>H<sub>2n+2</sub>]<sup>+</sup>, will be stabilized through the polarizability of substituents.<sup>1,2</sup> Therefore, the more easily polarized the alkane molecule, the more stable the final-state (charged molecule), and furthermore, the lower the ionization potential will be. That is to say, the substituent polarizability effect (final-state effect) can facilitate the ionization.

How to obtain the substituent polarizability effect for alkane molecule? Our previous work<sup>9</sup> indicated that the polarizability effect of alkyl substituents can be quantified by the Polarizability Effect Index (PEI). Thus, we can take

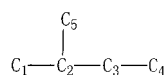
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each carbon atom of alkane molecule as the beginning one of the  $i$ th alkyl to calculate its PEI( $R_i$ ) respectively, and then we compute the geometric mean values of all the PEI( $R_i$ ) and obtain the Geometric Mean Polarizability Effect Index (GMPEI) of the alkane molecule by eq 1 to express its final-state effect. That is

$$\text{GMPEI} = [\prod_{i=1}^n \text{PEI}(R_i)]^{1/n} \quad (1)$$

In eq 1, the PEI( $R_i$ ) can be considered as a relative contribution of the  $i$ th alkyl group to the final-state effect or to the stabilizing positive charge. The GMPEI is the total final-state effect or relative stability for the charged alkane molecule. Because alkanes have about the same molecular electronegativities, the GMPEI can be directly employed to correlate their ionization potential.

The calculation of GMPEI for 2-methylbutane, for example, is described as follows:



First step: take  $\text{C}_1 - \text{C}_5$  as the beginning atom of alkyl group to calculate its PEI( $R_i$ ) respectively (more detail calculation, see ref 9).

$$\text{C}_1: \text{PEI}(R_1) = 1.00000 + 0.14053 + (2)(0.04813) + 0.02350 = 1.2603$$

$$\text{C}_2: \text{PEI}(R_2) = 1.00000 + (3)(0.14053) + 0.04813 = 1.4697$$

$$\text{C}_3: \text{PEI}(R_3) = 1.00000 + (2)(0.14053) + (2)(0.04813) = 1.3773$$

$$\text{C}_4: \text{PEI}(R_4) = 1.00000 + 0.14053 + 0.04813 + (2)(0.02350) = 1.2357$$

$$\text{C}_5: \text{PEI}(R_5) = 1.00000 + 0.14053 + (2)(0.04813) + 0.02350 = 1.2603$$

Second step: calculate the GMPEI of the molecule.

$$\text{GMPEI} = [\prod_{i=1}^n \text{PEI}(R_i)]^{1/n} = [1.2603 \times 1.4697 \times 1.3773 \times 1.2357 \times 1.2603]^{1/5} = 1.3177$$

As seen from the PEI( $R_i$ ) of 2-methylbutane, the order of relative contribution to the final-state effect or to the stabilizing positive charge is  $\text{C}_2 > \text{C}_3 > \text{C}_1 = \text{C}_5 > \text{C}_4$ .

The GMPEI of 2-methylbutane is 1.3177. Using the same calculating method, we got the GMPEI value of  $n$ -pentane 1.3051. While both 2-methylbutane and  $n$ -pentane have same number of carbon atoms, their GMPEI values are different. The GMPEI of 2-methylbutane is larger than that of  $n$ -pentane, which shows that the former has a larger final-state effect. In other words, the ionized 2-methylbutane molecule (with positive charge) is more stable than the ionized  $n$ -pentane molecule (with positive charge). Therefore, we can use the Geometric Mean Polarizability Effect Index

**Table 1.** GMPEI and Ip(eV) Values of Alkanes Bearing 1–8 Carbon Atoms

no.	alkane	GMPEI	Ip <sub>exp</sub> <sup>a</sup>	Ip <sub>eq2</sub> <sup>b</sup>	Ip <sub>AM1</sub> <sup>c</sup>	Ip <sub>Gau98</sub> <sup>d</sup>
1	methane	1	12.61 ± 0.01	12.60	13.30	14.83
2	ethane	1.1405	11.56 ± 0.02	11.56	11.73	13.24
3	propane	1.2187	10.95 ± 0.05	10.99	11.33	12.72
4	2-methylpropane	1.2807	(10.57)	10.53	11.29	12.44
5	butane	1.2694	10.53 ± 0.10	10.62	11.18	12.38
6	2,2-dimethylpropane	1.3360	(≤10.2)	10.13	11.52	12.26
7	2-methylbutane	1.3177	10.32 ± 0.05	10.26	11.17	12.09
8	pentane	1.3052	10.28 ± 0.10	10.35	11.12	12.12
9	2,2-dimethylbutane	1.3652	(10.06)	9.91	11.18	11.87
10	2,3-dimethylbutane	1.3576	(10.02)	9.97	11.01	11.86
11	2-methylpentane	1.3441	(10.12)	10.07	11.11	11.91
12	3-methylpentane	1.3469	(10.08)	10.05	11.04	11.85
13	hexane	1.3322	10.13	10.16	11.09	11.89
14	2,2,3-trimethylbutane	1.3989		9.67		
15	2,2-dimethylpentane	1.3848		9.77		
16	3,3-dimethylpentane	1.3897		9.73		
17	2,3-dimethylpentane	1.3806		9.80		
18	2,4-dimethylpentane	1.3757		9.84		
19	2-methylhexane	1.3642		9.92		
20	3-methylhexane	1.3678		9.90		
21	3-ethylpentane	1.3714		9.87		
22	heptane	1.3533	9.93 ± 0.10	10.00	11.08	11.72
23	2,2,3,3-tetramethylbutane	1.4359	9.8	9.39	10.98	11.49
24	2,2,3-trimethylpentane	1.4172		9.53		
25	2,3,3-trimethylpentane	1.4194		9.52		
26	2,2,4-trimethylpentane	1.4108	(9.86)	9.58	11.00	11.57
27	2,2-dimethylhexane	1.3995		9.66		
28	3,3-dimethylhexane	1.4058		9.62		
29	3-ethyl-3-methylpentane	1.4112		9.58		
30	2,3,4-trimethylpentane	1.4092		9.59		
31	2,3-dimethylhexane	1.3968		9.68		
32	3-ethyl-2-methylpentane	1.4011		9.65		
33	3,4-dimethylhexane	1.4000		9.66		
34	2,4-dimethylhexane	1.3947		9.70		
35	2,5-dimethylhexane	1.3906		9.73		
36	2-methylheptane	1.3803	(9.84)	9.80	11.05	11.60
37	3-methylheptane	1.3840		9.78		
38	4-methylheptane	1.3850		9.77		
39	3-ethylhexane	1.3887		9.74		
40	octane	1.3703	9.80 ± 0.10	9.88	11.07	11.59
41	nonane	1.3844	9.71 ± 0.10	9.77	11.07	11.48
42	decane	1.3963	(9.65)	9.69	11.07	11.40
43	undecane	1.4064	(9.56)	9.61	11.07	11.33

<sup>a</sup> From ref 13, values enclosed in parentheses are considered not to be well established. <sup>b</sup> Calculated by eq 2. <sup>c</sup> Calculated by quantum chemistry method AM1. <sup>d</sup> Calculated by ab initio quantum mechanical method (Gaussian 98, #HF/6-31G\*\* OPT).

to evaluate the ionization potential of alkanes. The GMPEI and ionization potential (Ip) values of some alkanes are listed in Table 1.

Because some of the experimental ionization potential values in Table 1 are not measured accurately (e.g. nos. 5, 9, 40, 41) and some of them are considered not to be well established<sup>13</sup>(see the values enclosed in parentheses), we chose the more accurate ionization potential values (Ip<sub>exp</sub>) of five compounds (nos. 1–3, 7, 13 of Table 1) to correlate with their GMPEI and obtained the following linear relationship:

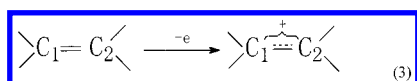
$$\text{Ip(eV)} = 19.941 - 7.3446\text{GMPEI}$$

$$F = 2110.67; s = 0.044(\text{eV}); r = 0.9993; n = 5 \quad (2)$$

There is a good linear correlation between ionization potential (Ip) and the Geometric Mean Polarizability Effect

Index (GMPEI). Equation 2 can be expected for evaluating ionization potential of alkanes (see the discussion section of this paper).

**Ionization Potential of Alkenes.** For alkenes, they all have the chemical formula  $C_nH_{2n}$  and the same molecular electronegativity 2.30 (Pauling electronegativity units). It is the most difference from alkane that the alkene has a  $\pi$  bond functional group  $C=C$  in its molecular structure. In general, the first ejected electron is considered from its  $\pi$  orbital. Obviously, the difference among alkene molecular ionization potential also is not resulted from their molecular electronegativities. Because the two carbon atoms on  $\pi$  bond have the same electronegativity, when ionization occurs in the  $\pi$  orbital, either carbon atom may carry fractional positive charge. That is

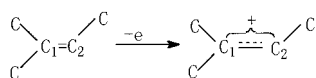


Positive charges on carbon atom  $C_1$  or  $C_2$  will polarize the alkyl substituents that connect with the charged carbon atom itself. In this case, taking the sum of  $PEI(R_i)$  for the carbon atom  $C_1$  and  $C_2$ , we get the  $\sum PEI(R_i)_{C1}$  and  $\sum PEI(R_i)_{C2}$ , respectively, and then obtain the Geometric Mean Polarizability Effect Index of  $\pi$  Bond (GMPEI $\pi$ ):

$$GMPEI\pi = [(\sum PEI(R_i)_{C1})(\sum PEI(R_i)_{C2})]^{1/2} \quad (4)$$

Here  $\sum PEI(R_i)_{C1}$  and  $\sum PEI(R_i)_{C2}$  express the relative contribution of alkyl substituents linked with  $C_1$  and  $C_2$  to the final-state effect or to the stabilizing positive charge, respectively. The GMPEI $\pi$  is the total final-state effect or relative stability of the charged alkene molecule.

For example, the calculation of GMPEI $\pi$  for 2-methyl-2-butene is described as follows:



$$C_1: \sum PEI(R_i)_{C1} = 1.0000 \times 2 + 1.1405 = 3.1405$$

$$C_2: \sum PEI(R_i)_{C2} = 1.0000 + 1.2810 = 2.2810$$

$$GMPEI\pi = [(\sum PEI(R_i)_{C1})(\sum PEI(R_i)_{C2})]^{1/2} = [3.1405 \times 2.2810]^{1/2} = 2.6765$$

That is, the GMPEI $\pi$  of 2-methyl-2-butene is 2.6765. Using the same calculating method, we got the GMPEI $\pi$  values of some alkenes (listed in Table 2).

As we did in correlating the ionization potential of alkane, here we chose some alkenes with one to four substituents on the  $\pi$  bond as model compounds, whose ionization potentials ( $Ip_{exp}$ )<sup>13</sup> have been measured more accurately. Correlating the ionization potentials of the six compounds (nos. 2, 3, 5, 6, 13, 25 in Table 2) with their GMPEI $\pi$  values, we obtained the expression

$$Ip(eV) = 10.846 - 0.79756 GMPEI\pi$$

$$F = 419.92; s = 0.059(eV); r = 0.9953; n = 6 \quad (5)$$

There is also a good linear correlation between ionization potential  $Ip$  and the Geometric Mean Polarizability Effect

**Table 2.** GMPEI $\pi$  and  $Ip$  (eV) Values of Some Alkenes

no.	alkene	GMPEI $\pi$	$Ip_{exp}^a$	$Ip_{eq5}^b$	$Ip_{AM1}^c$
1	ethylene	1.0000	10.5138 $\pm$ 0.0006	10.05	10.55
2	propene	1.5103	9.73 $\pm$ 0.02	9.64	9.99
3	1-butene	1.5951	9.55 $\pm$ 0.06	9.57	10.03
4	cis-2-butene	2.1405	9.11 $\pm$ 0.01	9.14	9.55
5	trans-2-butene	2.1405	9.10 $\pm$ 0.01	9.14	9.54
6	isobutene	1.9604	9.239 $\pm$ 0.003	9.28	9.67
7	cyclopentene	2.2810	9.01 $\pm$ 0.01	9.03	9.44
8	1-pentene	1.6228	9.51 $\pm$ 0.01	9.55	10.02
9	cis-2-pentene	2.2344	9.01 $\pm$ 0.03	9.06	9.51
10	trans-2-pentene	2.2344	9.04 $\pm$ 0.01	9.06	9.58
11	2-methyl-1-butene	2.0431	9.12 $\pm$ 0.01	9.22	9.71
12	3-methyl-1-butene	1.6796	9.52 $\pm$ 0.01	9.51	10.09
13	2-methyl-2-butene	2.6765	8.69 $\pm$ 0.01	8.71	9.26
14	cyclohexene	2.3292	8.945 $\pm$ 0.01	8.99	9.49
15	1-hexene	1.6469	9.44 $\pm$ 0.04	9.53	10.02
16	cis-2-hexene	2.2699	(8.97 $\pm$ 0.01)	9.04	9.51
17	trans-2-hexene	2.2699	(8.97 $\pm$ 0.01)	9.04	9.57
18	2-methyl-1-pentene	2.0769	(9.08 $\pm$ 0.01)	9.19	9.68
19	4-methyl-1-pentene	1.6225	9.45 $\pm$ 0.01	9.55	9.97
20	2-methyl-2-pentene	2.7577	(8.58)	8.65	9.24
21	4-methyl-cis-2-pentene	2.3273	8.98 $\pm$ 0.01	8.99	9.61
22	4-methyl-trans-2-pentene	2.3273	(8.97 $\pm$ 0.01)	8.99	9.62
23	2-ethyl-1-butene	2.1259	(9.06 $\pm$ 0.02)	9.15	9.72
24	2,3-dimethyl-1-butene	2.1259	(9.07 $\pm$ 0.01)	9.15	9.67
25	2,3-dimethyl-2-butene	3.2810	8.27 $\pm$ 0.01	8.23	8.96
26	1-heptene	1.6580	9.34 $\pm$ 0.10	9.52	10.02
27	trans-3-heptene	2.3650	(8.92)	8.96	9.62
28	1-octene	1.6657	9.43 $\pm$ 0.01	9.52	10.02
29	1-nonene	1.6712		9.51	10.01
30	1-decene	1.6755	9.42 $\pm$ 0.05	9.51	10.14

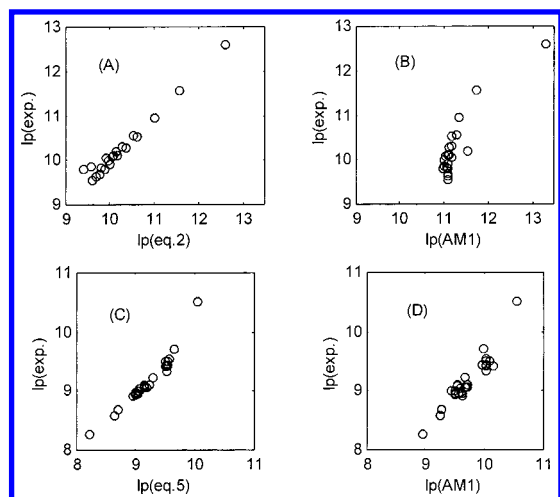
<sup>a</sup> From ref 13, values enclosed in parentheses are considered not to be well established. <sup>b</sup> Calculated by eq 5. <sup>c</sup> Calculated by quantum chemistry method AM1.

Index of  $\pi$  Bond (GMPEI $\pi$ ). This work estimates the ionization potentials of alkenes with eq 5 (see the discussion section of this paper).

### 3. DISCUSSION

**Influence of Polarizability Effect on the Ionization Potential of Alkane and Alkene.** The regression analysis results of eqs 2 and 5 indicate that GMPEI and GMPEI $\pi$  have good linear correlation with the ionization potential of alkanes and alkenes, respectively. Their intercepts can be considered as the characteristic constants related to the compound classes. For the alkane, the ejection of an electron is from its  $\sigma$  orbital, while from the  $\pi$  orbital for the alkene. The former needs more energy than the latter, so the intercept of eq 2 is larger than that of eq 5. The coefficients of the second term in the right of eqs 2 and 5 express the influence of molecular polarizability effect (final-state effect) on the ionization potentials of the mentioned compounds. The influence of the final-state effect on ionization potential is much larger in alkanes than in alkenes. Also known from eqs 2 and 5, GMPEI and GMPEI $\pi$  decrease the ionization potentials of alkanes and alkenes, respectively. It can be understood that, for a series of similar constructional molecules, the larger the molecular polarizability, and/or the more stable the charged molecule (final-state), the lower the molecular ionization potential will be.

Equations 2 and 5 are obtained by regression analysis only from a few of the compounds. Can they be used for evaluating the ionization potentials of other alkanes and alkenes? To test the reliability of the equations, we estimate the ionization potentials of some alkanes and alkenes by eqs 2 and 5, respectively, and further calculate their ionization potentials by semiempirical quantum chemistry method AM1



**Figure 1.** Plots of  $I_p(\text{exp.})$  vs  $I_p(\text{calc.})$  for alkanes and alkenes. For alkanes: (A):  $I_p(\text{exp.})$  vs  $I_p(\text{eq. 2})$ ; (B):  $I_p(\text{exp.})$  vs  $I_p(\text{AM1})$ . For alkenes: (C):  $I_p(\text{exp.})$  vs  $I_p(\text{eq. 5})$ ; (D):  $I_p(\text{exp.})$  vs  $I_p(\text{AM1})$ ;

(using MOPAC program packages in SYBL 6.7 of Tripos, Inc.). The obtained values of alkanes are listed in Table 1, and the values of alkenes are listed in Table 2. Comparing the calculated ionization potential values of 21 alkanes with the experimental literature ones<sup>13</sup> (see Table 1), the average absolute error between the experimental ( $I_{p,\text{exp.}}$ ) and calculated values ( $I_{p,\text{eq.2}}$ ) from eq 2 is only 0.084 (eV), and that between  $I_{p,\text{exp.}}$  and calculated values ( $I_{p,\text{AM1}}$ ) by AM1 method reaches 0.994(eV). The (A) and (B) in Figure 1 show the plots of calculated  $I_p$  values versus the experimental  $I_p$  values<sup>13</sup> for alkanes. For the 29 alkenes in Table 2, the average absolute error between the experimental ( $I_{p,\text{exp.}}$ )<sup>13</sup> and calculated values ( $I_{p,\text{eq.5}}$ ) from eq 5 is only 0.074 (eV), and that between  $I_{p,\text{exp.}}$  and calculated values ( $I_{p,\text{AM1}}$ ) by AM1 method reaches 0.543 (eV). The (C) and (D) in Figure 1 show the plots of calculated  $I_p$  values versus the experimental  $I_p$  values<sup>13</sup> for alkenes. Additionally, we have finished the ab initio quantum mechanical calculation of the alkane (see the  $I_{p,\text{Gau98}}$  values in Table 1), using the Gaussian 98 program package of Tripos Inc. at 6-31G\*\* basis set (#HF/6-31G\*\* OPT). This average error between the experimental  $I_{p,\text{exp.}}$  and calculated  $I_{p,\text{Gau98}}$  by Gaussian 98 reaches 1.81 (eV). Recently, Jursic<sup>14</sup> took SVWN density functional theory (DFT) to evaluate the ionization energy for some small alkane molecules and got an improved result. But “this method overestimates the ionization energies for simple molecular structures”.<sup>14</sup> Jursic even said “that HF ab initio methods are not able to compute accurate ionization energies”.<sup>14</sup> However we need to keep in mind that the ab initio calculation (or semiempirical) is from principles and is a powerful tool for computing ionization potential of organic compounds. It has the advantages without test data set. Of course, it still has some shortcomings, such as time-consuming, and sometimes unsatisfactory results. Thus, from a pragmatic point of view, it is worthy of searching a novel approach (nonquantum based) to calculate ionization potential for complicated alkanes and alkenes. From the results of Tables 1 and 2 and Figure 1, we can see the calculated ionization potential values by this work are in good agreement with the measured values. This work is simple and convenient and can supplement the quantum chemistry methods for calculating ionization potential of alkanes and alkenes.

**Table 3.** GMPEI $\pi$  and  $I_p$  (eV) Values of Some Alkynes

no.	alkyne	GMPEI $\pi$	$I_{p,\text{exp.}}^a$	$I_{p,\text{eq.6}}^b$	$I_{p,\text{AM1}}^c$
1	acetylene	1.0000	$11.400 \pm 0.0002$	11.09	11.44
2	propyne	1.5103	$10.37 \pm 0.01$	10.37	10.76
3	1-butyne	1.5951	$10.19 \pm 0.02$	10.25	10.67
4	2-butyne	2.1405	$9.59 \pm 0.03$	9.48	10.24
5	1-pentyne	1.6228	$10.10 \pm 0.01$	10.21	10.67
6	1-hexyne	1.6469	$10.03 \pm 0.05$	10.18	10.67
7	3,3-dimethyl-1-butyne	1.7639	$9.90 \pm 0.04$	10.01	10.72
8	1-octyne	1.6755	$(9.95 \pm 0.02)$	10.14	10.68
9	2-octyne	2.2998	$9.31 \pm 0.01$	9.26	10.19
10	3-octyne	2.3836	$9.22 \pm 0.01$	9.14	10.14
11	4-octyne	2.4009	$9.20 \pm 0.01$	9.11	10.14

<sup>a</sup> From ref 13, values enclosed in parentheses are considered not to be well established. <sup>b</sup> Calculated by eq 6. <sup>c</sup> Calculated by quantum chemistry method AM1.

For the alkynes, we can take the same method as in evaluating ionization potential of alkene to correlate their Geometric Mean Polarizability Effect Index of  $\pi$  Bond (GMPEI $\pi$ ) with their measured ionization potentials. The GMPEI $\pi$  and  $I_p$  values of some alkynes are listed in Table 3. Using these GMPEI $\pi$  and  $I_p$  values, we got the correlation equation

$$I_p(\text{eV}) = 12.505 - 1.41223 \text{ GMPEI}\pi$$

$$F = 162.22; s = 0.153(\text{eV}); r = 0.9733; n = 11 \quad (6)$$

There is still a good linear correlation between ionization potential  $I_p$  and the Geometric Mean Polarizability Effect Index of  $\pi$  Bond (GMPEI $\pi$ ) for alkynes. The calculated ionization potential values by eq 6 and by the AM1 method are all listed in Table 3. The results of Table 3 show that the calculated values in eq 6 are in more agreement with the measured values than that obtained by the AM1 method, the average absolute error between  $I_{p,\text{exp.}}$  and  $I_{p,\text{eq.6}}$  is 0.114 (eV), and that between  $I_{p,\text{exp.}}$  and  $I_{p,\text{AM1}}$  is 0.642 (eV).

It should be pointed out that there are still a few of the calculated values apart from the measured values obviously. They are compounds 2,2,3,3-tetramethylbutane and 2,2,4-trimethylpentane for alkanes, ethylene for alkenes, and acetylene for alkynes. The reason for causing this error is yet unknown and needs to be investigated deeply.

Further, we take all of the experimental potentials (including these values not to be well established<sup>13</sup>) in Tables 1 and 2 to make a correlation analysis with the GMPEI and GMPEI $\pi$ , respectively, and get the following results:

For alkanes:

$$I_p(\text{eV}) = 19.497 - 6.9851 \text{ GMPEI}$$

$$F = 688.28; s = 0.119(\text{eV}); r = 0.9865; n = 21 \quad (7)$$

For alkenes:

$$I_p(\text{eV}) = 10.956 - 0.8667 \text{ GMPEI}\pi$$

$$F = 383.55; s = 0.106(\text{eV}); r = 0.9666; n = 29 \quad (8)$$

The correlation coefficients between  $I_p$  and GMPEI or GMPEI $\pi$  in eqs 7 and 8 are less than that in eqs 2 and 5, but they are still in good linear correlations. As seen from eqs 6–8, the intercepts decrease as alkane (19.497), alkyne (12.505), and alkene (10.956), which is corresponding to the ionization potential order of alkane (ethane 11.56 eV) >



**Table 4.** Relationship between the Ionization Potential (Ip) and Some Well-Known Molecule Descriptors

descriptor <sup>17</sup>	regression equation	r	s	F	n
Randic index( $\chi$ )	11.6166–0.4812 $\chi$	0.8733	0.3546	61.04	21
valence connectivity index <sup>1</sup> $\chi^v$	11.6166–0.4812 <sup>1</sup> $\chi^v$	0.8733	0.3546	61.04	21
	11.2198–0.3635 <sup>1</sup> $\chi^v$	0.8749	0.2366	58.68	20 <sup>a</sup>
modify valence connectivity index ( <sup>n</sup> $\chi_n^v$ , this work)	11.0889–1.2752 <sup>n</sup> $\chi_n^v$	0.3154	0.6907	2.10	21
	7.0869+4.5171 <sup>n</sup> $\chi_n^v$	0.9197	0.1918	98.76	20 <sup>a</sup>
this work (GMPEI)	19.4966–6.9851GMPEI	0.9865	0.1193	688.28	21
Wiener numer (W)	10.6543–0.0075W	0.6046	0.5797	10.95	21
Hosoya index (Z)	10.5032–0.0100Z	0.4867	0.6358	5.90	21
Balaban index (J)	12.0960–0.7449J	0.8756	0.3515	62.44	21
Schultz index (MTI)	10.6576–0.0021MTI	0.6055	0.5792	11.00	21
Harary number (H)	11.4100–0.1638H	0.8632	0.3675	55.53	21

<sup>a</sup> Methane (CH<sub>4</sub>) is not included.

alkyne (acetylene 11.4 eV) > alkene (ethylene 10.51 eV). Also their coefficients of the second term (final-state effect) in the right follow the order of alkane (6.9851) > alkyne (1.4122) > alkene (0.8667), which decrease as the ionization potential order of compounds ethane, acetylene, and ethylene.

**Comparison GMPEI with Other Descriptors.** One may say that the descriptor GMPEI looks similar to the valence connectivity index <sup>m</sup> $\chi^v$  proposed by Kier and Hall.<sup>15</sup> They look alike, but they are indeed different kinds of descriptors. Their difference can be seen by comparing expression 1 with expression 9.

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

$$^m\chi^v = \sum \left[ \prod_{i=1}^{m+1} \delta_i^v \right]^{1/2} \quad (9)$$

Equation 1 gives a geometric mean value of all the vertexes (non-hydrogen atom) in a molecule, while eq 9 gives a sum value, in which each term consists of an m+1 consecutive vertex (non-hydrogen atom). Additionally, regardless of how many vertexes the molecule contains, only one GMPEI value can be calculated by eq 1. On the contrary, if eq 9 is used, there will be the following cases: (a) for the one vertex molecule, only one value, <sup>0</sup> $\chi^v$ , will be calculated; (b) for the two vertex molecule, two different values, <sup>0</sup> $\chi^v$  and <sup>1</sup> $\chi^v$ , can be computed; (c) When the molecule includes m vertexes, m values (<sup>0</sup> $\chi^v$ , <sup>1</sup> $\chi^v$ , <sup>2</sup> $\chi^v$ , ..., <sup>m-1</sup> $\chi^v$ ) will be obtained. On the other hand, each of the PEI(R<sub>i</sub>) values in eq 1 depends on the position of the i<sup>th</sup> vertex itself and other vertexes in molecule (see the calculation example of section 2 in this paper), while the  $\delta_i^v$  value of the i<sup>th</sup> vertex in eq 9 depends only on its valence-state in molecule.

For the alkane, the  $\delta_i^v$  values of units CH<sub>4</sub>, –CH<sub>3</sub>, –CH<sub>2</sub>–, >CH–, and >C< are 0, 1, 2, 3, and 4,<sup>16</sup> respectively. Taking these  $\delta_i^v$  values, we calculate the <sup>1</sup> $\chi^v$  values of the alkane molecule in Table 1 and make a correlation between their Ip<sub>exp.</sub> and <sup>1</sup> $\chi^v$ . The obtained correlation is not good (see the result in the first row in Table 4).

If we modify eq 9 to the pattern of eq 10

$$^n\chi_n^v = \left[ \prod_{i=1}^n \delta_i^v \right]^{-(1/n)} \quad (10)$$

and use the obtained <sup>n</sup> $\chi_n^v$  values to correlate with the Ip<sub>exp.</sub>

of alkanes in Table 1, the correlation is still worse than eq 7 (see the second and third rows in Table 4).

We also have noticed that there are many topological indices available. Some of them are well-known and important molecular descriptors, such as Wiener number (W), Hosoya index (Z), Randic index ( $\chi$ ), Balaban index (J), Schultz index (MTI), Harary number (H), and so on,<sup>17</sup> which have been applied widely in QSPR studies. Here we take these indices (values taken from ref 17) as variable and make linear regression analysis with a single parameter against the experimental ionization potentials of alkanes in Table 1. The results are listed in Table 4. The results of Table 4 show that the GMPEI parameter has the best correlation with the experimental ionization potential of alkanes.

From the above discussion, it can be concluded that the polarizability effect is an important factor causing the difference of ionization potential among alkanes, alkenes, and alkynes. The method developed by this paper is suitable for evaluating the ionization potential of alkanes, alkenes, and alkynes.

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