

On Molecular Polarizability: 3. Relationship to the Ionization Potential of Haloalkanes, Amines, Alcohols, and Ethers

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The relationship between the ionization potential and the parameters molecular electronegativity and molecular polarizability for haloalkanes, amines, alcohols, and ethers was investigated. There is no good linear correlation between the ionization potential I_p and molecular electronegativity χ_{eq} alone for these compounds. I_p can be modeled well with three parameters: χ_{eq} , polarizability effect index (PEI) of an alkyl group, and atomic polarizability (P). Further, a single expression for predicting the I_p values of aldehydes, esters, nitriles, and carboxylic acids was developed: $I_{p(RZ)}(eV) = I_{p(MeZ)} + 1.4544\Delta\chi_{eq} - 1.6435\Delta\Sigma PEI(Ri)$. Here $I_{p(MeZ)}$ is the experimental ionization potential of monosubstituted methane MeZ. $\Delta\chi_{eq}$ and $\Delta\Sigma PEI(Ri)$ are the difference in the molecular electronegativity and the difference in the polarizability effect index of alkyl groups attached to the functional group Z between molecules MeZ and RZ, respectively.

1. INTRODUCTION

It is known that the electronegativity, χ , of any chemical species (an atom or molecule) is the negative of its chemical potential,^{1,2} μ , obtained from density functional theory as in eq 1

$$\chi = -\mu = -(\partial E/\partial N)_v \quad (1)$$

where E is the exact Hohenberg and Kohn energy functional for an N -electron system characterized by an external potential v . According to the principle of electronegativity equalization, if free flow is allowed in a molecule, electrons go from a region of high chemical potential to a region of low chemical potential until both regions have the same chemical potential value.³ It results in an equal electronegativity for each atom in a molecule. This equal electronegativity is also known as molecular electronegativity, which corresponds to equalization of chemical potentials in a compound. Molecular electronegativity can be calculated by different methods, such as geometric mean,³ harmonic mean,⁴ and weighted mean.⁵ Electronegativity equalization methods have been widely used for calculating atomic charges in molecules,^{1,4,5} and the atomic charges thus obtained were used for evaluating bond energy^{6,7} and core binding energy of carbon atoms.^{8–10} Equation 1 might seem to predict that the ionization potentials of different kinds of organic compounds may be estimated directly by using their molecular electronegativities. In fact, if one makes a correlation of the molecular electronegativities with their ionization potentials, as is done in the next section of this paper, he will obtain no good results. The reason, we think, may be that eq 1 expresses only the chemical potential of chemical species in the case of a fixed external potential v and no rearrangement of charge within a molecule. Indeed, molecular ionization takes place in the influence of an external electric field, which may polarize the molecule. The impor-

tance of polarizability could be based on the rearrangement of charge within a molecule when an electron is removed from an electronegative center such as a halogen atom. If a neutral molecule is easy to polarize in an external field, it should also be easy to shift electronic charge from the alkyl group to the halogen atom when the molecule is ionized, thereby stabilizing the cation and lowering I_p . Therefore there are at least two factors, molecular electronegativity and molecular polarizability, affecting its ionization. This paper investigates the relation between the ionization potential and the parameters molecular electronegativity and molecular polarizability for haloalkanes, amines, alcohols, and ethers.

2. MODELING FOR THE IONIZATION POTENTIAL OF HALOALKANES, AMINES, ALCOHOLS, AND ETHERS

Ionization Potential of Haloalkanes. First, we take haloalkane RX (R is the alkyl group, X stands for halogen atoms F, Cl, Br, and I) as model compounds because their functional group is relatively simple. The molecular electronegativities of 27 haloalkanes (in Table 1) were calculated by Bratsch's electronegativity equalization method⁴ (harmonic mean, with Pauling electronegativity units). For example, the molecular electronegativity χ_{eq} of CH_3F is calculated as follows.

It is known that the electronegativities are 2.20, 2.55, and 3.98 for H, C, and F elements, respectively. Thus the CH_3F molecular electronegativity is

$$\chi_{eq} = \frac{5}{\frac{1}{2.55} + \frac{3}{2.20} + \frac{1}{3.98}} = 2.4912$$

Using the molecular electronegativity values, χ_{eq} , thus obtained and the experimental ionization potentials,¹¹ I_p , we get the regression eq 2:

$$I_p (eV) = -38.9085 + 20.8957\chi_{eq} \quad (2)$$

$$F = 81.8047, \quad s = 0.43, \quad r = 0.8752, \quad n = 27$$

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Table 1. Ionization Potential Ip (eV) and Parameters χ_{eq} , PEI, and P for Haloalkanes

no.	compd	χ_{eq}	PEI	P^a	Ip_{exp}^a	Ip_{calc}^b	$Ip_{exp} - Ip_{calc}$
1	MeF	2.4912	1.0000	0.5570	12.850	12.785	0.065
2	MeCl	2.4128	1.0000	2.1800	11.300	11.334	-0.034
3	EtCl	2.3714	1.1405	2.1800	10.970	10.929	0.041
4	<i>n</i> -PrCl	2.3531	1.1887	2.1800	10.820	10.758	0.062
5	<i>i</i> -PrCl	2.3531	1.2810	2.1800	10.780	10.701	0.079
6	<i>n</i> -BuCl	2.3427	1.2122	2.1800	10.670	10.664	0.006
7	<i>s</i> -BuCl	2.3427	1.3292	2.1800	10.650	10.591	0.059
8	<i>i</i> -BuCl	2.3427	1.2368	2.1800	10.660	10.649	0.011
9	<i>t</i> -BuCl	2.3427	1.4216	2.1800	10.610	10.534	0.076
10	MeBr	2.3882	1.0000	3.0500	10.530	10.689	-0.159
11	EtBr	2.3565	1.1405	3.0500	10.290	10.358	-0.068
12	<i>n</i> -PrBr	2.3424	1.1887	3.0500	10.180	10.220	-0.040
13	<i>i</i> -PrBr	2.3424	1.2810	3.0500	10.075	10.163	-0.088
14	<i>n</i> -BuBr	2.3343	1.2122	3.0500	10.125	10.144	-0.019
15	<i>s</i> -BuBr	2.3343	1.3292	3.0500	9.980	10.071	-0.091
16	<i>i</i> -BuBr	2.3343	1.2368	3.0500	10.090	10.128	-0.038
17	<i>t</i> -BuBr	2.3343	1.4216	3.0500	9.890	10.013	-0.123
18	<i>n</i> -AmBr	2.3292	1.2260	3.0500	10.100	10.096	0.004
19	MeI	2.3455	1.0000	4.7000	9.540	9.496	0.044
20	EtI	2.3303	1.1405	4.7000	9.330	9.292	0.038
21	<i>n</i> -PrI	2.3235	1.1887	4.7000	9.260	9.210	0.050
22	<i>i</i> -PrI	2.3235	1.2810	4.7000	9.170	9.153	0.017
23	<i>n</i> -BuI	2.3196	1.2122	4.7000	9.210	9.166	0.044
24	<i>s</i> -BuI	2.3196	1.3292	4.7000	9.090	9.093	-0.003
25	<i>i</i> -BuI	2.3196	1.2368	4.7000	9.180	9.150	0.030
26	<i>t</i> -BuI	2.3196	1.4216	4.7000	9.020	9.035	-0.015
27	<i>n</i> -AmI	2.3171	1.2260	4.7000	9.190	9.138	0.052

^a Taken from ref 11. ^b Calculated by eq 4.

The coefficient, $r(0.8752)$, of eq 2 indicates a poor linear correlation between Ip and χ_{eq} . It disagrees with what is suggested by eq 1. As mentioned, the ionization of a haloalkane molecule is due to the rearrangement of charge within a molecule, that is, the distribution of charge on an alkyl group in a cation is different from that in a neutral molecule. Therefore its ionization relates not only to its molecular electronegativity but also to its molecular polarizability.

Generally, because of a pair of nonbonded electrons on the halogen atom, the first ionization takes place on the halogen atom of the haloalkane molecule RX:



The effect of molecular polarizability on the ionization potential consists of two parts: the polarizability of the halogen atom itself and the polarizability of the alkyl group attached to the halogen atom. The former is measured by atomic polarizability P (unit of 10^{-24} cm^3 , for F, Cl, Br, and I atoms, their P values are 0.557, 2.18, 3.05, and 4.7 respectively),¹¹ while the latter may be estimated with the polarizability effect index (PEI)¹² of the alkyl group. Taking the EtCl molecule for example, the Cl atomic polarizability P is $2.18(10^{-24} \text{ cm}^3)$, and the PEI of group Et is 1.1405 based on part 1 of this work.¹²

Now let the ionization potential of haloalkane be a function of molecular electronegativity (χ_{eq}), polarizability effect index (PEI) of the alkyl group, and halogen atomic polarizability (P) (listed in Table 1). We get eq 4 by multiple linear regression.

$$Ip \text{ (eV)} = -5.3872 + 7.6622\chi_{eq} - 0.62348PEI - 0.52436P \quad (4)$$

$$F = 1451.99, \quad s = 0.066, \quad r = 0.9974, \quad n = 27$$

Clearly, eq 4 is much better than eq 3 for calculating the ionization potential of haloalkane. It also shows that the molecular polarizability is an important factor affecting the molecular ionization.

Ionization Potential of Amines, Alcohols, and Ethers.

Amines, alcohols, and ethers all have a pair of nonbonded electrons on nitrogen or oxygen atom. Therefore their first ionization will take place on the N atom of amines or the O atom of alcohols and ethers. As in dealing with haloalkane, we relate their ionization potentials to the same three parameters: χ_{eq} , PEI, and P . However, amines, alcohols, and ethers are different from haloalkane in that the halogen atom only bears one group. The N atom of amines or O atom of alcohols and ethers connects with more than one group. Thus the sum, $\Sigma PEI(Ri)$, of the PEI values of all groups must be used. Additionally, there is a hydrogen atom H attached to the N and O atom in amines and alcohols. Its PEI value is not known. How large is the PEI value of an H atom? Taft¹³ calculated polarizability effect parameter values σ_α by quantum chemistry for five alkyl groups, Me, Et, *n*-Pr, *i*-Pr, and *t*-Bu, and obtained -0.35, -0.49, -0.54, -0.62, and -0.75, respectively. It is found that there is a good linear correlation between σ_α and PEI values¹² for these alkyl groups:

$$\sigma_\alpha = 0.5899 - 0.9449PEI \quad (5)$$

$$s = 0.0054, \quad r = 0.9995, \quad n = 5$$

Using eq 5 and Taft's polarizability effect parameter value $\sigma_\alpha = 0$ of H atom, we obtain the PEI(H) value, 0.6243, of H atom. This paper uses $PEI(H) = 0.6243$ to calculate the $\Sigma PEI(Ri)$ values of amines and alcohols.

For example, in CH_3NH_2 , its N atomic polarizability P is $1.10 (10^{-24} \text{ cm}^3)$,¹¹ $\Sigma PEI(Ri) = PEI(\text{CH}_3) + 2PEI(H) = 1.0000 + 2(0.6243) = 2.2486$. The values of parameters χ_{eq} , $\Sigma PEI(Ri)$, and P of nitrogen or oxygen atom for amines, alcohols, and ethers are listed in Table 2. Based on the experimental ionization potentials¹¹ of Table 2 and the three parameters, we get the multiregression eq 6:

$$Ip \text{ (eV)} = -0.32784 + 6.0703\chi_{eq} - 1.3301 \Sigma PEI(Ri) - 1.6347P \quad (6)$$

$$F = 458.24, \quad s = 0.130, \quad r = 0.9924, \quad n = 25$$

There is a good linear correlation between ionization potential Ip and the three parameters, χ_{eq} , $\Sigma PEI(Ri)$, and P . The result also shows that the PEI(H) value 0.6243 of hydrogen atom H is reasonable.

Both eqs 4 and 6 indicate that the molecular electronegativity increases the ionization potential, while the atomic polarizability and the polarizability effect index of alkyl group decrease the ionization potential. It can be understood that the higher the molecular electronegativity, the lower the molecular chemical potential, and the higher the Ip . On the other hand, the larger the atomic polarizability and the group's polarizability are, the more stable is the molecular cation formed in ionization. In fact, the molecular electronegativity cannot include the effect of molecular polarizability on its ionization. For example, the isomers *n*-BuCl, *i*-BuCl, *s*-BuCl, and *t*-BuCl have the same molecular electronega-

Table 2. Ionization Potential I_p (eV) and Parameters χ_{eq} , PEI, and P for Amines, Alcohols, and Ethers

no.	compd	χ_{eq}	SPEI(Ri)	P^a	I_{pexp}^a	I_{pcalc}^b	$I_{pexp} - I_{pcalc}$
1	MeOH	2.3990	1.6243	0.8020	10.84	10.76	0.08
2	EtOH	2.3670	1.7648	0.8020	10.49	10.38	0.11
3	PrOH	2.3513	1.8130	0.8020	10.10	10.22	-0.12
4	<i>i</i> -PrOH	2.3513	1.9053	0.8020	10.15	10.10	0.05
5	BuOH	2.3420	1.8365	0.8020	10.04	10.13	-0.09
6	MeOMe	2.3670	2.0000	0.8020	9.98	10.07	-0.09
7	EtOEt	2.3420	2.2810	0.8020	9.60	9.54	0.06
8	PrOPr	2.3314	2.3774	0.8020	9.27	9.35	-0.08
9	(<i>i</i> -Pr) ₂ O	2.3314	2.5620	0.8020	9.20	9.10	0.10
10	MeNH ₂	2.3381	2.2486	1.1000	8.97	9.08	-0.11
11	EtNH ₂	2.3282	2.3891	1.1000	8.86	8.83	0.03
12	PrNH ₂	2.3229	2.4373	1.1000	8.78	8.73	0.05
13	<i>i</i> -PrNH ₂	2.3229	2.5296	1.1000	8.72	8.61	0.11
14	BuNH ₂	2.3196	2.4608	1.1000	8.71	8.68	0.03
15	<i>s</i> -BuNH ₂	2.3196	2.5778	1.1000	8.70	8.53	0.17
16	<i>i</i> -BuNH ₂	2.3196	2.4854	1.1000	8.70	8.65	0.05
17	<i>t</i> -BuNH ₂	2.3196	2.6702	1.1000	8.64	8.40	0.24
18	Me ₂ NH	2.3282	2.6243	1.1000	8.24	8.52	-0.28
19	Et ₂ NH	2.3196	2.9053	1.1000	8.01	8.09	-0.08
20	Pr ₂ NH	2.3158	3.0017	1.1000	7.84	7.94	-0.10
21	(<i>i</i> -Pr) ₂ NH	2.3158	3.1863	1.1000	7.73	7.69	0.04
22	Bu ₂ NH	2.3135	3.0487	1.1000	7.69	7.86	-0.17
23	Me ₃ N	2.3229	3.0000	1.1000	7.82	7.98	-0.16
24	Et ₃ N	2.3135	3.4215	1.1000	7.50	7.38	0.12
25	Pr ₃ N	2.3128	3.5660	1.1000	7.23	7.17	0.06

^a Taken from ref 11. ^b Calculated by eq 6.

tivity, but they have different ionization potentials. It results from the different polarizability of the alkyl group attached to atom Cl.

When we make a multiregression between the experimental ionization potentials and the parameters χ_{eq} , $\Sigma PEI(Ri)$, and P for all 52 compounds in Tables 1 and 2, we obtain eq 7:

$$I_p \text{ (eV)} = 10.247 + 1.4544\chi_{eq} - 1.6435 \Sigma PEI(Ri) - 0.65527P \quad (7)$$

$$F = 835.91, \quad s = 0.158, \quad r = 0.9906, \quad n = 52$$

Equation 7 shows that there is still a good correlation between the I_p and the parameters χ_{eq} , $\Sigma PEI(Ri)$, and P . If we relate their ionization potentials with only its molecular electronegativity, we get the expression 8:

$$I_p \text{ (eV)} = 0.94468 + 3.3557\chi_{eq} \quad (8)$$

$$F = 39.23, \quad s = 0.845, \quad r = 0.6631, \quad n = 52$$

From eqs 2 and 8, we can conclude that the molecular ionization potential cannot be estimated accurately by the single parameter molecular electronegativity.

3. DISCUSSION

Equation 7 can be used to estimate the ionization potential for haloalkanes, amines, alcohols, and ethers. For instance, the calculated (experimental) ionization potential values of cyclo-C₄H₈O and cyclo-C₅H₁₀O are 9.41(9.42)¹¹ and 9.32-(9.25)¹¹ (eV), respectively. Besides the previous kinds of compounds, can eq 7 also be used to predict ionization potentials of other monosubstituted paraffins (RZ)? As we know, when the functional group Z includes an unsaturated chemical bond, such as -CHO, -CO-, -CN, the ionization

of molecule RZ will take place on its group Z. The applicability of eq 7 to RZ with multiatom Z is limited because of the difficulty in determining the polarizability P of such a Z group. Usually, the ionization potential of the relatively simple molecule MeZ can be easily measured for a series of monosubstituted paraffins RZ. We now develop a relative method of evaluating the ionization potential from this. That is, if the functional group Z is given, we take monosubstituted methane MeZ as a reference compound (using its experimental ionization potential $I_{p(MeZ)}$ to estimate $I_{p(RZ)}$ of other monosubstituted paraffins) and then obtain eq 9 from eq 7:

$$I_{p(RZ)} \text{ (eV)} = I_{p(MeZ)} + 1.4544\Delta\chi_{eq} - 1.6435\Delta\Sigma PEI(Ri) \quad (9)$$

here $\Delta\chi_{eq}$ and $\Delta\Sigma PEI(Ri)$ are the difference of molecular electronegativity and difference of polarizability effect index of alkyl groups attached to the functional group Z between molecule MeZ and RZ, respectively. Obviously, we no longer need the parameter atomic polarizability of the group Z. For the example MeCHO and EtCHO, their functional groups are both CHO, and the calculated molecular electronegativities are 2.4195 and 2.3841, respectively. Thus $\Delta\chi_{eq} = 2.3841 - 2.4195 = -0.0354$ and $\Delta\Sigma PEI(Ri) = PEI(Et) - PEI(Me) = 1.1405 - 1.0000 = 0.1405$ for EtCHO. The experimental ionization potential of MeCHO is 10.2 (eV).¹¹ From eq 9, we get the ionization potential of EtCHO, $I_{p(EtZ)} \text{ (eV)} = 10.2 + 1.4544(-0.0354) - 1.6435(0.1405) = 9.92 \text{ (eV)}$. The calculated value is in good agreement with its measured value 9.98 (eV).¹¹ The calculated ionization potential values I_p (eV) for several kinds of compounds are listed in Table 3.

To test the accuracy of eq 9, we compare the calculated ionization potential values of 34 compounds with the experimental literature values.¹¹ The results listed in Table 3 show that eq 9 gives a good estimate of ionization potential values for the mentioned paraffins. The average absolute error between the experimental and calculated values is only 0.065 (eV) for these compounds. Further, we carried out a regression analysis between the experimental ionization potentials and the parameters $I_{p(MeZ)}$, $\Delta\chi_{eq}$, and $\Delta\Sigma PEI(Ri)$ for 41 applicable compounds from Table 3 and then obtained eq 10:

$$I_{p(RZ)} \text{ (eV)} = 0.42998 + 0.95839I_{p(MeZ)} + 1.7471\Delta\chi_{eq} - 1.5584\Delta\Sigma PEI(Ri) \quad (10)$$

$$F = 1984.20, \quad s = 0.065, \quad r = 0.9969, \quad n = 41$$

There is still a good correlation in eq 10. Its standard deviation is equal to the average absolute error of eq 9. Therefore we can expect the same precision of I_p predicted by eqs 9 and 10. The results predicted by eq 10 were also listed in Table 3. Clearly, eq 9 has less coefficients than eq 10, and the former is more convenient than the latter in application.

From eqs 7, 8, and 9 and the discussion above, we can conclude that the ionization potentials of monosubstituted paraffins RZ cannot be modeled accurately with molecular electronegativity alone. They can, however, be estimated well from the parameters $\Delta\chi_{eq}$ and $\Delta\Sigma PEI(Ri)$ based on the measured ionization potential of reference compounds MeZ

Table 3. Ionization Potentials Ip (eV) and Relative Parameters for Monosubstituted Paraffins

no.	compd ^a	χ_{eq}	$\Delta\Sigma PEI(Ri)$	Ip_{exp}^b	Ip_{calc}^c	Ip_{calc}^d
1	MeCHO*	2.4195	0.0000	10.2		10.20
2	EtCHO	2.3841	0.1405	9.98	9.92	9.92
3	<i>n</i> -PrCHO	2.3795	0.1887	9.86	9.83	9.84
4	<i>i</i> -PrCHO	2.3795	0.2810	9.74	9.68	9.70
5	<i>n</i> -BuCHO	2.3540	0.2122	9.82	9.76	9.76
6	<i>s</i> -BuCHO	2.3540	0.3292		9.56	9.57
7	<i>i</i> -BuCHO	2.3540	0.2368	9.71	9.72	9.72
8	<i>t</i> -BuCHO	2.3540	0.4216		9.41	9.42
9	<i>n</i> -AmCHO	2.3462	0.2260		9.72	9.72
10	MeCOMe*	2.3841	0.0000	9.69		9.72
11	EtCOMe	2.3795	0.1405	9.5	9.45	9.49
12	<i>n</i> -PrCOMe	2.3540	0.1887	9.37 ± 0.02	9.34	9.37
13	<i>i</i> -PrCOMe	2.3540	0.2810	9.30 ± 0.02	9.18	9.23
14	<i>n</i> -BuCOMe	2.3462	0.2122	9.35	9.29	9.32
15	<i>s</i> -BuCOMe	2.3462	0.3292		9.09	9.14
16	<i>i</i> -BuCOMe	2.3462	0.2368	9.30	9.25	9.28
17	<i>t</i> -BuCOMe	2.3462	0.4216	9.17 ± 0.03	8.94	8.99
18	<i>n</i> -AmCOMe	2.3406	0.2260	9.33	9.26	9.29
19	EtCOEt	2.3540	0.2810	9.32 ± 0.01	9.18	9.20
20	MeCN*	2.4226	0.0000	12.2		12.12
21	EtCN	2.3821	0.1405	11.84	11.91	11.83
22	<i>n</i> -PrCN	2.3625	0.1887	11.67 ± 0.05	11.80	11.72
23	<i>i</i> -PrCN	2.3625	0.2810		11.65	11.58
24	<i>n</i> -BuCN	2.3509	0.2122		11.78	11.66
25	<i>s</i> -BuCN	2.3509	0.3292		11.59	11.48
26	<i>i</i> -BuCN	2.3509	0.2368		11.74	11.63
27	<i>t</i> -BuCN	2.3509	0.4216		11.43	11.34
28	<i>n</i> -AmCN	2.3432	0.2260		11.71	11.63
29	MeCO ₂ H*	2.5128	0.0000	10.693 ± 0.03		10.68
30	EtCO ₂ H	2.4525	0.1405	10.24 ± 0.03	10.37	10.35
31	<i>n</i> -PrCO ₂ H	2.4195	0.1887	10.16 ± 0.05	10.25	10.22
32	<i>i</i> -PrCO ₂ H	2.4195	0.2810	10.02 ± 0.05	10.09	10.08
33	<i>n</i> -BuCO ₂ H	2.3985	0.2122		10.16	10.18
34	<i>s</i> -BuCO ₂ H	2.3985	0.3292		9.97	10.00
35	<i>i</i> -BuCO ₂ H	2.3985	0.2368		10.12	10.14
36	<i>t</i> -BuCO ₂ H	2.3985	0.4216		9.82	9.85
37	<i>n</i> -AmCO ₂ H	2.3841	0.2260		10.13	10.10
38	MeO ₂ CMe*	2.4525	0.0000	10.27 ± 0.02		10.27
39	EtO ₂ CMe	2.4195	0.0482	10.11 ± 0.02	10.14	10.14
40	<i>n</i> -PrO ₂ CMe	2.3985	0.0717	10.04 ± 0.03	10.07	10.07
41	<i>i</i> -PrO ₂ CMe	2.3985	0.0963	9.99 ± 0.03	10.03	10.03
42	<i>n</i> -BuO ₂ CMe	2.3841	0.0855	10.01	10.03	10.02
43	<i>s</i> -BuO ₂ CMe	2.3841	0.1199	9.91 ± 0.03	9.97	9.97
44	<i>i</i> -BuO ₂ CMe	2.3841	0.0952	9.97	10.01	10.00
45	<i>t</i> -BuO ₂ CMe	2.3841	0.1446		9.93	9.92
46	<i>n</i> -AmO ₂ CMe	2.3735	0.0945		10.00	9.98
47	MeO ₂ CH*	2.5128	0.0000	10.815 ± 0.005		10.79
48	EtO ₂ CH	2.4525	0.0482	10.61 ± 0.01	10.65	10.61
49	<i>n</i> -PrO ₂ CH	2.4195	0.0717	10.54 ± 0.01	10.56	10.52
50	<i>i</i> -PrO ₂ CH	2.4195	0.0963		10.52	10.48
51	<i>n</i> -BuO ₂ CH	2.3985	0.0855	10.5 ± 0.02	10.51	10.46
52	<i>s</i> -BuO ₂ CH	2.3985	0.1199		10.45	10.41
53	<i>i</i> -BuO ₂ CH	2.3985	0.0952	10.46 ± 0.02	10.49	10.45
54	<i>t</i> -BuO ₂ CH	2.3985	0.1446		10.41	10.37
55	<i>n</i> -AmO ₂ CH	2.3841	0.0945		10.47	10.42
56	MeSH*	2.3096	0.0000	9.44		9.48
57	EtSH	2.3081	0.1405	9.28	9.21	9.26
58	PrSH	2.3076	0.1887	9.19	9.13	9.18
59	BuSH	2.3070	0.2122	9.14	9.09	9.14
60	MeSMe	2.3081	0.3757	8.69	8.82	8.89
61	EtSMe	2.3076	0.5162	8.55	8.59	8.67
62	EtSEt	2.3070	0.6567	8.47	8.36	8.45

^a The compounds with “*” are the reference compounds. ^b Taken from ref 11. ^c Calculated by eq 9. ^d Calculated by eq 10.

for a series of compounds. The molecular polarizability is an important factor affecting the ionization potential of monosubstituted paraffins.

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