

## On Polarizability Effect of Alkyl Substituent

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The relative polarizability effect of alkyl substituent can be conveniently obtained by calculating the so-called Polarizability Effect Index (PEI) value, proposed firstly in our laboratories,  $PEI = \sum (a_i/N_i^2)$ , where  $a_i$  is the polarizability of primary units  $\text{CH}_3$ ,  $\text{CH}_2$ -,  $\text{CH}$ < and  $>\text{C}$ -, and the  $N_i$  is the carbon atom number from reaction site to the primary unit. By using the PEI and atomic charge in a molecule, the ionization potential of alkyl halide, the enthalpy of reaction for the gas-phase addition of a proton to an alcohol or ether (proton affinity), the gas-phase basicity of alcohols or ethers (proton affinity), and gas-phase acidity of alcohols can be quantitatively modeled by the two-parameter expression equation.

## INTRODUCTION

Polarizability effect is one of the four primary kinds of substituent effects including field effect, electronegativity effect, polarizability effect and resonance effect.<sup>1</sup> It arises from the stabilization provided by the probe charge or dipole inducing a dipole in the substituent.<sup>2</sup> Now, organic chemists can explain the gas-phase acidities, and basicities of alkyl-substituted amines, mercaptanes, alcohols and ethers with it. There are different methods to evaluate the polarizability effect. Gasteiger et al.<sup>3</sup> proposed effective polarizability as substituent polarizability effect contributions, but the derivation of a polarizability scale has proved difficult. Taft<sup>1</sup> and Topsom<sup>2</sup> got the polarizability potentials ( $\sigma_a$ ) from the quantum chemical method. However, it is not easy to see the change law and to predict the relative magnitude of the polarizability for alkyl substituents with their method. In this work, a new approach being both simple and having physical meaning was proposed to quantify the polarizability of alkyl substituents.

## POLARIZABILITY EFFECT INDEX (PEI)

As we know, the stabilizing energy,  $E$ , caused by polar-

izability effect for a substituent interacting with a point charge  $q$  is:

$$E = -(aq^2) / (2Dr^4) \quad (1)$$

where  $a$  is the polarizability of the substituent,  $D$  is the effective dielectric constant, and  $r$  the distance of the point charge  $q$  to the center of substituent polarizability. For an alkyl substituent  $R$ , the total stabilizing energy  $E$  (Eq 1) can be taken as the sum of contributions from primary units, such as  $\text{CH}_3$ ,  $\text{CH}_2$ -,  $\text{CH}$ < and  $>\text{C}$ -, which consists of three C-H bonds, two C-H and one C-C bonds, one C-H and two C-C bonds, and three C-C bonds, respectively. For instance, the total polarizability energy  $E$  of *n*-butyl and *i*-butyl can be calculated as follows. In Equation 1,  $a_i$  is the polarizability of  $i$ th primary unit, and  $r_i$  the distance of the charge ( $q$ ) to the  $i$ th carbon atom. Therefore, we can rewrite the Eq. 1 as Eq. 2 for alkyl substituent (Also see Fig. 1).

$$E = -(q^2/2D) (\sum a_i/r_i^4) \quad (2)$$

How to determine the  $a_i$  and  $r_i$  of Eq. 2? Here, we take the sum of polarizability of all bonds in the  $i$ th primary unit as the  $a_i$  value. That is, for  $\text{CH}_3$ ,  $\text{CH}_2$ -,  $\text{CH}$ < and  $>\text{C}$ -, their  $a_i$  are  $\alpha_{\text{Me}} = 3\alpha_{\text{C-H}}$ ,  $\alpha_{\text{CH}_2} = 2\alpha_{\text{C-H}} + \alpha_{\text{C-C}}$ ,  $\alpha_{\text{CH}} = \alpha_{\text{C-H}} + 2\alpha_{\text{C-C}}$ , and  $\alpha_{>\text{C}} = 3$

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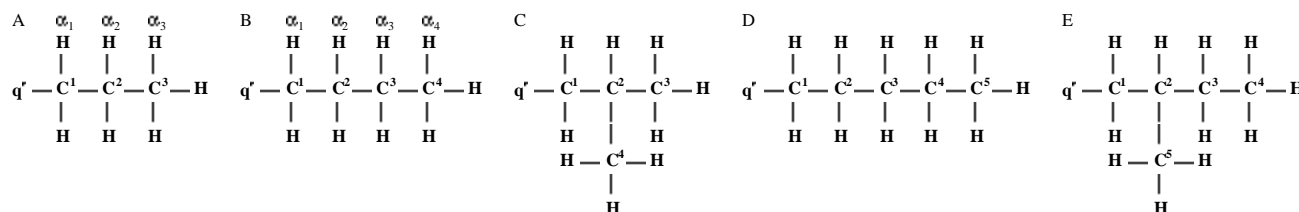


Fig. 1. Schematics for calculation of the total polarizability energy  $E$  of propyl (a), n-butyl (b), iso-butyl (c), n-amyl (pentyl, d) and iso-amyl (e).

$\alpha_{C-C}$ , respectively. According to Miller's work,<sup>4</sup> the  $\alpha_{C-H} = 1/4 \alpha_{CTE} + \alpha_H$ , and the  $\alpha_{C-C} = 2 \times (1/4) \times \alpha_{CTE}$ . From the experimental polarizabilities of H atom ( $\alpha_H = 0.353 \cdot \text{\AA}^3$ ) and C atom ( $sp^3$  hybridization,  $\alpha_{C-H} = 1/4 \alpha_{CTE} = 1.443 \cdot \text{\AA}^3$ ), we got the  $a_i$  of  $CH_3$ ,  $CH_2$ -,  $CH<$  and  $>C-$  are 2.156, 2.159, 2.162 and 2.164 ( $\text{\AA}^3$ ), respectively. The  $a_i$  of all four primary units are approximately equal to 2.16 ( $\text{\AA}^3$ ).

As to the  $r_i$  of Eq. 2, it is difficult to calculate the absolute values. But we may use their relative distance for discussing the  $E$  value or order of different alkyl substituents. Statistically, the mean-square end-to-end distance  $\langle L_0^2 \rangle$  of a molecular chain  $-(CH_2)_N-$  is proportional to the number  $N$  of repeating unit  $CH_2$ .

$$\langle L_0^2 \rangle = kN_i \quad (3)$$

Therefore, we propose that the  $r_i^2$  of Eq. 2 is also approximately equal to  $kN_i$

$$r_i^2 = kN_i \quad (4)$$

where  $N_i$  is the carbon atom number from the point charge to the  $i$ th primary unit in molecular chain. Now, substituting, the  $kN_i$  for  $r_i^2$ , we lead to Eq. 5 from Eq. 2.

$$\begin{aligned} E &= -(q^2/2D) (\sum_i a_i/k^2 N_i^4) = E \\ &= -(q^2/2D k^2) (\sum_i a_i/N_i^4) = K \cdot \text{PEI} \end{aligned} \quad (5)$$

For a given system, the  $q$  and  $D$  were given. Let  $K = -q^2/(2Dk^2)$ , thus, Eq. 5 becomes Eq. 6.

$$E = K (\sum_i a_i/N_i^4) = K \cdot \text{PEI} \quad (6)$$

We call this sum term  $\sum (a_i/N_i^4)$  the Polarizability Effect Index (PEI). To the chain alkyl substituent, when the polarizability of the  $i$ th primary unit is taken as  $a_i = 2.16$  the  $E$  of Eq. 6 may be expressed as Eq. 7:

$$\begin{aligned} E &= K (\sum_i a_i/N_i^4) = K (\sum_i 2.16/k^2 N_i^4) \\ &= K' (\sum_i 1/N_i^4) = K \cdot \text{PEIA} \end{aligned} \quad (7)$$

where  $K' = 2.16 K$ , PEIA is the PEI of alkyl substituent. In this case, we can directly predict the polarizability or order of the alkyl groups using PEIA value. Table 1 reports PEIA values of some substituents.

## RESULTS AND DISCUSSION

Table 1 shows that the PEIA value increases as the carbon atom number increases for the normal alkyl substituents, but the increment decreases rapidly as the carbon atom number increases. In fact, there is a limit value,  $\lim_{N \rightarrow \infty} (\sum_i 1/N_i^4) = \pi^2/6$ . When the carbon atom numbers are the same, the more the groups bonded to the carbon radical, the bigger the PEIA

Table 1. Values of Some Alkyl Substituents

No.	Group	PEIA	No.	Group	PEIA	No.	Group	PEIA
01	CH <sub>3</sub>	1.0000	08	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> -	1.5274	15	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> -	1.4861
02	CH <sub>3</sub> CH <sub>2</sub> -	1.2500	09	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> -	1.5398	16	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -	1.8611
03	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -	1.3611	10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> -	1.5498	17	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> -	1.6944
04	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> -	1.4236	11	(CH <sub>3</sub> ) <sub>2</sub> CH-	1.5000	18	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> )-	1.6736
05	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> -	1.4636	12	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> -	1.4722	19	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CH-	1.7222
06	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> -	1.4914	13	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )-	1.6111	20	(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> )-	1.7222
07	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> -	1.5118	14	(CH <sub>3</sub> )C-	1.7500			

value is. For instance, the PEIA value order is:  $i\text{-Pr} > n\text{-Pr}$ ;  $t\text{-Bu} > s\text{-Bu} > i\text{-Bu} > n\text{-Bu}$ .

$$\sigma_{\text{R}} = 0.1803 - 0.5322\text{PEI} \text{ or } \text{PEI} = 0.3388 - 2.8393\sigma_{\text{R}} \\ r = 1.000 \quad (\text{A})$$

With comparison to Taft's<sup>1</sup> polarizability potential from Eq. 7, we predict there will be a linear relation between the PEIA value of alkyl substituents and Taft's polarizability potential  $\sigma_{\text{R}}$ . Regressing or plotting PEIA versus  $\sigma_{\text{R}}$ , the regression Equation (A) and the linear figure (omitted, due to its poor information and the article's limitation of space) shows there is an excellent linear correlation between PEIA and  $\sigma_{\text{R}}$ . Based on Equation (A) and H atom polarizability potential<sup>1</sup> ( $\sigma_{\text{R}}(\text{H}) = 0.00$ ), we got the H atom PEIA value being 0.3387 (this is done in order to discuss the problem conveniently).

### Ionization Potential of Alkyl Halide

The first application of PEIA is the ionization potential  $I_{\text{p}}$  of Alkyl Halide RX ( $X = \text{I, Br and Cl}$ ). In general, the first electron ionized from RX is the p-electron of X atom in molecule RX.<sup>5</sup> For a given X atom ( $X = \text{Cl, Br or I}$ ),  $I_{\text{p}}(\text{RX})$  depends on two factors, one is the charge on the X atom, the other is the polarizability of alkyl substituent R. In this work,

we use Bratsch's<sup>6</sup> method of equalized electronegativity to calculate the charge on the X atom. Since the polarizability energy of R is proportional to the PEIA (see Eq. 7), we use PEIA values to express the relative polarizability order of group R.

Calculated input data for the regression analysis are recorded in Table 2, along with the experimental values. The  $I_{\text{p}}$  data on alkyl halide were processed by regression analysis jointly against either a single parameter or combinations of two, and their relevant results are collected in Table 3. It is readily seen that the correlations with the best results are those of the multiple linear regression (MLR) analyses with two-parameter models those based on  $q_{\text{X}}$  ( $X = \text{I, Br and Cl}$ ) along with statistics (Eqs. 8, 9 and 10, Table 3, entries 3, 6 and 9), we can reproduce the  $I_{\text{p}}$  data set of RX satisfactorily. They are also recorded in Table 2.

$$I_{\text{p}}(\text{RI}) = 10.94 - 0.603 \sum(1/N_i^2) + 6.77q_{\text{I}} - \\ n = 9, r = 0.999, s = 0.0077 \quad (8)$$

$$I_{\text{p}}(\text{RBr}) = 11.89 - 0.764 \sum(1/N_i^2) + 3.19q_{\text{Br}} - \\ n = 9, r = 0.999, s = 0.0093 \quad (9)$$

$$I_{\text{p}}(\text{RCl}) = 14.89 - 0.589 \sum(1/N_i^2) + 12.66q_{\text{Cl}} - \\ n = 8, r = 0.982, s = 0.0520 \quad (10)$$

The regression expressions are entirely consistent with

Table 2. Experimental and Calculated Ionization Potential  $I_{\text{p}}(\text{eV})$  and Molecular Parameters

No	Mol. R-X RX(I, Br, Cl)	$q_{\text{X}}(\text{I})$	$q_{\text{X}}(\text{Br})$	$q_{\text{X}}(\text{Cl})$	PEIA	Ionization potential					
		$q_{\text{I}}$	$q_{\text{Br}}$	$q_{\text{Cl}}$		X=I, exptl. <sup>a</sup>	calcd. (8)	X=Br, exptl. <sup>a</sup>	calcd. (9)	X=Cl, exptl. <sup>a</sup>	calcd. (10)
1	MeI	-0.118	-0.185	-0.236	1.0000	9.54	9.54	10.54	10.54	11.31	11.31
2	EtI	-0.24	-0.204	-0.250	1.2500	9.33	9.35	10.28	10.28	11.01	10.99
3	n-PrI	-0.127	-0.209	-0.255	1.3611	9.26	9.26	10.18	10.18	10.88	10.86
4	n-BuI	-0.128	-0.211	-0.259	1.4236	9.21	9.21	10.15	10.13	10.84	10.77
5	n-AmI	-0.129	-0.213		1.4636	9.19	9.18	10.10	10.09		
6	i-PrI	-0.127	-0.209	-0.255	1.5000	9.17	9.17	10.075	10.077	10.78	10.78
7	i-BuI	-0.128	-0.211	-0.259	1.4722	9.18	9.18	10.09	10.09	10.66	10.74
8	s-BuI	-0.128	-0.211	-0.259	1.6111	9.09	9.10	9.98	9.99	10.65	10.66
9	t-BuI	-0.128	-0.211	-0.259	1.7500	9.02	9.02	9.89	9.88	10.61	10.58

<sup>a</sup> Data of MeBr–n-BuBr and MeCl–n-BuCl taken from Ref. 7, others from Ref. 8

Table 3. Results of Correlation Analysis for Ionization Potential with  $q_{\text{X}}$  and PEIA of RX ( $X = \text{I, Br, Cl}$ )

Entry	Ionization Potential	RI: $r^a$	$s^b$	Entry	Ionization Potential	$r^a$	$s^b$	Entry	Ionization Potential	$r^a$	$s^b$
1	$q_{\text{I}}$	0.891	$7.2 \times 10^{-2}$	4	$q_{\text{Br}}$	0.875	$9.6 \times 10^{-2}$	7	$q_{\text{Cl}}$	0.943	$8.4 \times 10^{-2}$
2	$\text{PEIA}' = \sum(1/N_i^2)$	0.996	$1.5 \times 10^{-2}$	5	$\text{PEIA}' = \sum(1/N_i^2)$	0.995	$1.9 \times 10^{-2}$	8	$\text{PEIA}' = \sum(1/N_i^2)$	0.960	$7.0 \times 10^{-2}$
3	$q_{\text{I}}, \sum(1/N_i^2)$	0.999	$7.7 \times 10^{-3}$	6	$q_{\text{Br}}, \sum(1/N_i^2)$	0.999	$9.3 \times 10^{-3}$	9	$q_{\text{Cl}}, \sum(1/N_i^2)$	0.982	$5.2 \times 10^{-2}$
n	RX=RI	(n=9)			RX=RBr	n=9			RX=RCl	n=8	

<sup>a</sup> Relation coefficient. <sup>b</sup> Standard deviation in eV. <sup>c</sup> Number of compound in data set.

intuition and experience, in that the negative signs of the  $PEIA = \sum(1/N_i^2)$  coefficients indicate that an increase in polarizability increases the cation stabilization and results in lower  $I_p$ . In contrast, the positive sign of the  $q_x$  coefficients reflects the fact that the halogen atom in  $RX$  ( $X = Cl, Br, I$ ) is difficult to be ionized.

According to the "Principle of Electronegativity Equalization",<sup>9</sup> the atoms of the same element in an isomer carry the same charge (e.g. the I atom in  $n\text{-PrI}$  carries the same charge). However, they do not have the same ionization potential  $I_p$  indeed. Why? It is due to the different polarizability of the isomeric groups. The regression models can reproduce the observed differences in  $I_p$  between isomeric molecules (e.g.,  $n\text{-PrX}/i\text{-PrX}$ ;  $n\text{-BuX}/i\text{-BuX}/s\text{-BuX}/t\text{-BuX}$ ). In each case the difference is due mainly to polarizability influences.

### Proton Affinity of Alcohols and Ethers

From the discussion above, it may be predicted that the proton affinity (PA) of protonation reaction (Eq. 11) of alcohols

and ethers will increase as the Polarizability Effect Index (PEI),  $PEI = \sum(a_i/N_i^2)$ , of groups R and R' increases, and decrease as the positive charge  $q_0$  on an oxygen atom in the ROR' molecule increases. Using the charge on the oxygen atom  $q_0$ , PEI,  $\sum(a_i/N_i^2)$  of alcohols and ethers, and the experimental PA values<sup>10-12</sup> in Table 4, we obtained the following calculated results from the linear multiple regression analysis:



$$PA = 128.4 - 129.7q_0 + 5.333$$

$$n = 23, r = 0.996, s = 0.67 \text{ kcal/mol} \quad (12)$$

The expression (Eq. 12) is consistent with the physical interpretation. By the comparison between experimental and calculated PA values in Table 4, it is seen that Eq. 12 is successful.

The usefulness of the expression can be further tested through its ability to predict PA's of molecules. Several such

Table 4. Experimental and Calculated Proton Affinity values and Molecular Parameters<sup>a</sup>

No.	Molecule		$q_0$	$PEIA = \sum(a_i/N_i^2)$	Proton Affinity(PA)	
	ROR':	R R'			exptl. <sup>b</sup>	calcd. <sup>c</sup>
1	Me	H	-0.3026	2.8916	182.5	183.1
2	Et	H	-0.3119	3.4316	187.8	187.2
3	n-Pr	H	-0.31695	3.6716	189.6	189.0
4	n-Bu	H	-0.3192	3.8066	190.2	190.1
5	i-Pr	H	-0.3165	3.9716	192.0	190.6
6	t-Bu	H	-0.3192	4.5101	193.4	193.9
7	Me	Me	-0.3119	4.3200	191.1	191.9
8	Et	Me	-0.3165	4.8600	195.2	195.4
9	n-Pr	Me	-0.3192	5.1000	196.1	197.0
10	n-Bu	Me	-0.3210	5.2350	197.3	198.0
11	i-Pr	Me	-0.3192	5.4000	198.6	198.6
12	t-Bu	Me	-0.3210	5.9400	201.1	201.7
13	1-Admantyl	Me	-0.3179	6.9295	206.0	206.6
14	Et	Et	-0.3192	5.4000	198.5	198.6
15	i-Pr	Et	-0.3210	5.9400	202.3	201.7
16	t-Bu	Et	-0.3223	6.4800	205.1	204.8
17	n-Pr	n-Pr	-0.3223	5.8800	201.1	201.6
18	i-Pr	i-Pr	-0.3223	6.4800	204.8	204.3
19	t-Bu	t-Bu	-0.3229	2.5600	212.0	210.8
20	(CH <sub>2</sub> ) <sub>2</sub> O	Cyclic ethers	-0.2967	3.6011	186.4	186.1
21	(CH <sub>2</sub> ) <sub>3</sub> O		-0.3069	4.4634	193.2	193.2
22	(CH <sub>2</sub> ) <sub>4</sub> O		-0.3124	5.2203	197.6	196.8
23	(CH <sub>2</sub> ) <sub>5</sub> O		-0.3157	5.5596	198.5	199.0

<sup>a</sup>  $q_0$  calculated from Ref. 6;  $\sum(a_i/N_i^2)$  is the sum of alkyl groups and H atom (for ROH). For H atom of ROH, the  $1/N_i^2 = 0.3387$  (see text for detail), and here, the value of  $a_i/N_i^2 = 2.16 \times 0.3387$ .

<sup>b</sup> Data taken from Ref. 10.

<sup>c</sup> Calculated from Eq. 12.



examples not included in the compilation of data originally used for the multiple linear regression (MLR) analysis are available. Thus the PA values calculated from regression analysis are available. Thus the PA value calculated from Eq. 12 (experimental value), for *n*-Bu<sub>2</sub>O is 203.2(203.7), that for *s*-Bu<sub>2</sub>O is 207.6(209.0), that for *n*-Am<sub>2</sub>O is 204.3(205.2), and that for *i*-Pr<sub>2</sub>O-, *t*-Bu<sub>2</sub>O- is 207.8(208.8).

### Gas-Phase Acidity of Alcohols

In fact, the gas-phase acidity of alcohols can be expressed by the gas-phase basicity of alkoxide ion in reaction of Eq. 13.



The  $\Delta G^\circ$  (basicity) of Eq. 13 is equal to the (acid) of alcohol ROH. Similar to the PA of alcohol, we take the  $\Delta G^\circ$  (basicity) as a positive value. That is, the more the  $\Delta G^\circ$  (basicity) of Eq. 13 is, the stronger the basicity of alkoxide ion RO<sup>-</sup> is, and the weaker the acidity of alcohol ROH is. The smaller  $\Delta G^\circ$  (basicity) value indicates the stronger acidity of alcohol ROH.

The  $\Delta G^\circ$  (basicity) of Eq. 13 can be described by Eq. 14.

$$\Delta G^\circ (\text{basicity}) = 359.7 - 43.39 q_o - 4.588 \sum (1/N_i^2) \\ n = 7, r = 0.998, s = 0.45 \text{ kcal/mol} \quad (14)$$

where  $q_o$  is the charge on an oxygen atom of alkoxide ion RO<sup>-</sup>. The relevant molecular parameters and (basicity) values (experimental and calculated from Eq. 14) are recorded in Table 5. The results show that the calculated  $\Delta G^\circ$  (basicity) values correspond to better experimental values.

In Eq. 14, the signs of and coefficients all are negative. It indicates that a positive charge of an oxygen atom in RO<sup>-</sup> and polarizability of all groups (R) decrease the basicity of

alkoxide ion RO<sup>-</sup>. In other words, they all increase the acidity of alcohol ROH. This case is still consistent with the physical interpretation. The positive charge of an oxygen atom in RO results in decreasing the ability of combination between the RO<sup>-</sup> and H<sup>+</sup>; it increases the stabilization of the negative charge in RO<sup>-</sup>, and results in a lower  $I_p$ . Therefore, the polarizability of R also decreases the basicity of RO<sup>-</sup> and increases the acidity of ROH.

### CONCLUSION

The relative polarizability of an alkyl substituent can be predicted by the very simple method that reflects both the atomic property (polarizability) and molecular structure in this work. Starting from the molecular static characteristics (molecular equalized electronegativity and the charge on a given atom) and the dynamic property (polarizability), we may explain and predict quantitatively the ionization potential, gas-phase acidity and basicity for some substituted hydrocarbon compounds. The present approach can be used more widely than that stated above. These applications will be reported in the author's future papers.

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### Key Words

Polarizability effect index (PEI); Alkyl substituent; Proton affinity; Acidity; Basicity.

Table 5. Experimental and Calculated (basicity,  $\Delta G^\circ$ ) Values of RO<sup>-</sup> and Molecular Parameters<sup>a</sup>

RO <sup>-</sup>	RO <sup>-</sup>	$q_o$	$\sum (1/N_i^2)$	Basicity	$\Delta G^\circ$
				(exptl <sup>b</sup> )	(calcd. <sup>c</sup> )
1	HO <sup>-</sup>	-0.6099	0.3387	384.5	384.6
2	MeO <sup>-</sup>	-0.4380	1.0000	374.0	373.8
3	EtO <sup>-</sup>	-0.3922	1.2500	371.4	371.0
4	<i>n</i> -PrO <sup>-</sup>	-0.3747	1.3611	369.5	369.7
5	<i>i</i> -PrO <sup>-</sup>	-0.3747	1.5000	368.5	369.1
6	<i>t</i> -BuO <sup>-</sup>	-0.3649	1.7500	368.0	367.5
7	<i>s</i> -BuO <sup>-</sup>	-0.3649	1.6111	367.6	368.1

<sup>a</sup>  $q_o$  calculated from Ref. 6.

<sup>b</sup> Data taken from Ref. 10.

<sup>c</sup> Calculated from Eq. 12.



## REFERENCES

1. Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.
2. Topsom, R. D. *Prog. Org. Chem.* **1987**, *16*, 125.
3. Gasteiger, J.; Hutchings, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 6489-6495.
4. Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533-8542.
5. Streitwieser, A. *Prog. Phys. Org. Chem.* **1963**, *1*, 21.
6. Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101.
7. Sun, Yukun; Xu, Guangxian; Li, Lemin, *Chem. J. Chinese Univ.* **1982**, *3*(3), 389; Robinson, J. W. *Handbook of Spectroscopy*; 1974, Vol. 1.
8. Weast, R. C. *Handbook of Chemistry and Physics*; 65th ed.; CRC Press INC., 1984-1985.
9. Sanderson, R. T. *Science* **1951**, *114*, 670.
10. Abboud, J. L. M.; Elguero, J.; Liotard, D.; Essefar, M. H.; El Mouhtadi, M.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1990**, 565.
11. Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*(3), 695.
12. Taft, R. W.; Koppel, L. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047-2052.

