

# Substituent Effects on Thermochemical Properties of Free Radicals. New Substituent Scales for C-Centered Radicals

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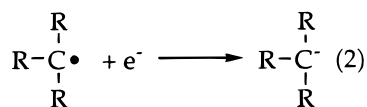
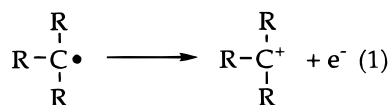
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In this work, we have analyzed substituent effects on ionization potentials and electron affinities of C-centered radicals in terms of operational atomic contributions. The analysis was based on ionization potential data for 48 C-centered radicals and electron affinity data for 20 C-centered radicals. For both sets of data, the correlation between predicted numbers and experimental data was good ( $R = 0.98$ ). Based on these operational atomic parameters, additive substituent constants have also been derived, and equations for prediction of ionization potentials and electron affinities of C-centered radicals are presented.

## INTRODUCTION

C-centered radicals are important intermediates in radical synthesis as well as in a number of industrial and naturally occurring processes, e.g. polymerization, cracking of oil, combustion, bleaching of pulp, atmospheric chemistry, lipid peroxidation, and oxidation of peptides.<sup>2,3</sup> The redox reactivity of C-centered radicals varies from strongly reducing to strongly oxidizing, depending on the structure of the radical and the substituent pattern. The thermochemical properties that, to a large extent, govern the reactivity of radicals are the ionization potential and electron affinity and their solution counterparts, the one-electron oxidation and reduction potentials (reactions 1 and 2).



In general, the rate of addition of radicals to alkenes is correlated to the electron affinity of the radical,<sup>4</sup> and the rate of oxidation of alkyl radicals correlates to the ionization potential of the radical.

Linear free energy relationships are useful tools in predicting and understanding thermochemical properties and reaction kinetics for numerous chemical systems.<sup>5</sup> In radical chemistry, linear free energy relationships have been found to successfully describe substituent effects on aromatic systems<sup>6</sup> but not to the same extent on nonaromatic radicals. Very frequently, substituent effects on nonaromatic radicals are described qualitatively rather than quantitatively, while aromatic systems often can be described by the Hammett equation using the Hammett or Brown substituent constants,  $\sigma$  and  $\sigma^+$ , respectively.<sup>5,6</sup> For nonaromatic systems, substituent scales of the same generality as the Hammett and

Brown scales have not been available. Attempts have been made to derive an operational substituent scale for the one-electron reduction potential of peroxy radicals.<sup>7</sup>

Recently, a new additive model of the inductive (field) effect was presented<sup>8,9</sup> and successfully applied on a number of different chemical systems.<sup>10</sup> In this method, a theoretical scheme for calculation of Taft's inductive substituent constant was introduced. However, this approach has, until now, not been tested on radical systems. In this work, we have used this approach, jointly with the Model of Frontier Steric Effect<sup>11,12</sup> allowing calculation of steric Taft's constants, to quantitatively study substituent effects on the redox properties of C-centered radicals (ionization potentials and electron affinities).

## METHODS

The theoretical approaches used in this work have been described in detail elsewhere.<sup>8–12</sup> In short, it has been established that both steric and inductive effects of any substituent at any reactive center can be described at an atomic level of additivity. The "Model of the Frontier Steric Effect" and "Additive Model of Inductive Effect" allow determination of the corresponding  $R_s$  steric and  $\sigma^*$  inductive constants (in the format of Taft's  $E_s$  and  $\sigma^*$  scales) of substituents on the basis of the fundamental characteristics of the constituent atoms

$$R_s = -30 \log \left( 1 - \sum_{i=1}^n \frac{R_{A_i}^2}{14r_i^2} \right) \quad (3)$$

where  $n$  is the number of atoms in the substituent,  $R_A$  is the atomic radius,  $r$  is the direct distance from the  $i$ th atom of the substituent to the reaction center, and

$$\sigma^* = \sum_{i=1}^n \frac{\sigma_{A_i}}{r_i^2} \quad (4)$$

$\sigma_A$  is an empirical parameter reflecting the ability of an atom to attract (or donate) electrons (depending on the nature and the valence state of the atom).

The values of  $\sigma_A$  have been calculated for a wide range of elements in various valence states by substitution of the empirical Taft's  $\sigma^*$  constants in eq 4 for 422 substituents, and solving it for 28  $\sigma_A$  atomic values within the least-squares solution of equations<sup>13</sup>

$$\sigma_j^* = a_{j1}\sigma_{A_1} + a_{j2}\sigma_{A_2} + \dots + a_{jN}\sigma_{A_N} \quad (5)$$

where  $\sigma^*$  is the inductive constant of the substituent,  $a_{jN}$  is the sum of the corresponding  $1/r^2$  items, related to a certain type of atom. In the absence of this atom in the substituent  $j$ , the  $a_{jN}$  value is set equal to 0.  $N$  variables were determined.

These additive approaches have made it possible to describe, with high accuracy, the steric and inductive constants of a large number of substituents giving the following correlations (eqs 6<sup>11</sup> and 7<sup>13</sup>)

$$R_S = -1.702(\pm 0.032) + 0.730(\pm 0.022)E_S \quad (6)$$

$$N = 35, \quad R = 0.9854, \quad S_0 = 0.141$$

where  $R_S$  is the steric constant calculated by eq 3 and  $E_S$  is the corresponding Taft's steric parameters

$$\sigma_{\text{theor}}^* = 0.014(\pm 0.010) + 0.993(\pm 0.006)\sigma_{\text{exper}}^* \quad (7)$$

$$N = 422, \quad R = 0.993, \quad S = 0.149$$

where  $\sigma_{\text{theor}}^*$  values for more than 400 substituents were calculated on the basis of atomic  $\sigma_A$  parameters.

Furthermore, for a broad selection of elements,  $\sigma_A$  constants correlate to the difference in electronegativity between a given element and the reaction center,  $\Delta\chi_{i-\text{RC}}$ , reflecting the driving force for the electron density displacement and, with the square of the covalent radius of the element,  $R_i$ , reflecting the ability to delocalize the charge (eq 8).<sup>8-10</sup>

$$\sigma_A = 7.84\Delta\chi_{i-\text{RC}}R_i^2 \quad (8)$$

This is in good agreement with the magnitude and sign of inductive constants. Thus, this additive model clarifies the physical meaning of the inductive effect by describing it in terms of pure electrostatic interactions of bonded atoms.

The steric model has the simple physical meaning of mechanical shielding of the reaction center by atoms of the substituents, corresponding to eq 3.<sup>10-12</sup>

These easily understandable additive models developed on the basis of empirical data (Taft's inductive and steric constants) have already become useful tools for quantitative interpretation of electronic and steric intramolecular effects.

## RESULTS AND DISCUSSION

When applying linear free energy relationships on ionization potentials it should be kept in mind that the gas-phase ionization potential is the enthalpy of ionization at 0 K. However, the ionization entropy and temperature corrections are assumed to be fairly small and are therefore neglected.

Bearing this in mind, we have analyzed the ionization potential (IP) and electron affinity (EA) of C-centered radicals in terms of possible electronic and steric effects on the basis of the free energy linearity (LFE) principle

$$\Delta H \approx \Delta G = \Delta G_E + \Delta G_S \quad (9)$$

where the electronic effect,  $E$ , can include both inductive and resonance contributions. At the atomic level of additivity eq 9 can be expressed as

$$\Delta G = a_0 + a_1\sum\sigma + a_2\sum R_S \quad (10)$$

where  $\sum\sigma$  is the sum of the electronic contributions (inductive and resonance) and  $\sum R_S$  is the sum of the steric contributions. According to the formalism of correlation analysis we can introduce relative scales both for EA and IP (eqs 11 and 12)

$$\text{EA} - \text{EA}_0 = b_1\sum\sigma + b_2\sum R_S \quad (11)$$

$$\text{IP} - \text{IP}_0 = b_3\sum\sigma + b_4\sum R_S \quad (12)$$

where  $\text{EA}_0$  and  $\text{IP}_0$  correspond to the electron affinity and ionization potential, respectively, of the methyl radical.

It is noteworthy that eq 3 can be transformed into a more simple expression (eq 13), since for small  $x$  values,  $\log(1 - x)$  is linear in  $x$  (the term is  $\sum(R_i^2/4r_i^2)$  small for most substituents).<sup>11,12</sup> Thus we can write the steric parameter  $R'_S$  as

$$R'_S = \sum_{i=1}^n \frac{R_i^2}{r_i^2} \quad (13)$$

If we combine eqs 4 and 8 into eq 14

$$\sigma^* = 7.84 \sum_{i=1}^n \frac{\Delta\chi_i R_i^2}{r_i^2} \quad (14)$$

we can express the inductive constants of substituents through the parameters of the constituent atoms.

It is obvious now that both steric and inductive effects of substituents, explored at the atomic level of additivity, are functions of atomic  $r^{-2}$  values.

There is however one problem; the electronegativity of the radical carbon atom is not known, thus, we are not able to calculate the inductive effect of substituents at carbon-radical reaction center using eq 8. Furthermore, resonance stabilization of the system cannot be accounted for by the present model.

To avoid these problems we have instead determined overall operational atomic parameters,  $e_i$ , which could contain both steric and electronic (inductive and resonance, provided that the resonance effect is also proportional to  $r^{-2}$ ). We have used the least-squares procedure to determine overall  $e_i$  values.

$$\text{IP(EA)}_{\text{R}} - \text{IP(EA)}_{\text{CH}_3} = \sum_{i \in \text{R}} \frac{e_i}{r_i^2} \quad (15)$$

**Table 1.** Operational Atomic Parameters,  $e^+$ , Derived from Ionization Potentials of C-Centered Radicals

atom	$e^+$	atom	$e^+$
C (sp <sup>3</sup> )	$-1.86 \pm 0.11$	C (sp)	$-0.8 \pm 0.39$
H	$-0.25 \pm 0.04$	N (sp)	$5.89 \pm 2.13$
N	$-6.15 \pm 0.26$	Cl	$-1.91 \pm 0.19$
O	$-3.77 \pm 0.27$	Br	$-2.73 \pm 0.23$
C (aromatic)	$-1.45 \pm 0.14$	F	$-0.78 \pm 0.10$
C (sp <sup>2</sup> )	$-1.78 \pm 0.14$	S	$-6.61 \pm 0.58$

**Table 2.** Operational Atomic Parameters,  $e^-$ , Derived from Electron Affinities of C-Centered Radicals

atom	$e^-$	atom	$e^-$
C (sp <sup>3</sup> )	$-0.256 \pm 0.14$	Cl	$2.22 \pm 0.17$
H	$-0.01 \pm 0.04$	Br	$2.08 \pm 0.23$
C (aromatic)	$0.60 \pm 0.06$	C (sp <sup>2</sup> )	$0.51 \pm 0.37$
F	$1.04 \pm 0.08$	O	$-0.15 \pm 0.44$

**Table 3.** Experimental Ionization Potentials and Estimated Relative Ionization Potentials of C-Centered Radicals<sup>a</sup>

no.	radical	IP <sup>14</sup> (eV)	IP - IP <sub>Me</sub> (eV)	(IP - IP <sub>Me</sub> ) <sub>est</sub> (eV)	residuals (eV)
1	H <sub>3</sub> C•	9.84	0	-0.63	0.63
2	CH <sub>3</sub> CH <sub>2</sub> •	8.12	-1.72	-1.36	-0.35
3	C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> •	8.09	-1.75	-1.69	-0.05
4	C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> •	8.02	-1.82	-1.84	0.02
5	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> •	7.93	-1.91	-2.02	0.11
6	(CH <sub>3</sub> ) <sub>2</sub> CH•	7.37	-2.47	-2.1	-0.36
7	(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )CH•	7.25	-2.59	-2.43	-0.15
8	(CH <sub>3</sub> ) <sub>3</sub> C•	6.7	-3.14	-2.83	-0.30
9	cyclo-C <sub>3</sub> H <sub>5</sub> •	8.18	-1.66	-1.97	0.31
10	cyclo-C <sub>4</sub> H <sub>7</sub> •	7.54	-2.3	-2.43	0.13
11	cyclo-C <sub>5</sub> H <sub>9</sub> •	7.21	-2.63	-2.73	0.10
12	H <sub>2</sub> NCH <sub>2</sub> •	6.29	-3.55	-3.38	-0.16
13	CH <sub>3</sub> NHCH <sub>2</sub> •	5.9	-3.94	-3.74	-0.19
14	(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> •	5.7	-4.14	-4.10	-0.04
14	CH <sub>3</sub> (NH <sub>2</sub> )CH•	5.7	-4.14	-4.12	-0.02
16	(CH <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> )C•	5.4	-4.44	-4.85	0.41
17	H <sub>2</sub> C=CHCH <sub>2</sub> •	8.18	-1.66	-1.58	-0.07
18	(CH <sub>2</sub> =C)(CH <sub>3</sub> )CH <sub>2</sub> •	7.9	-1.94	-1.88	-0.05
19	H <sub>2</sub> C=CHCH <sub>2</sub> CH <sub>2</sub> •	8.04	-1.8	-1.78	-0.01
20	H <sub>2</sub> C=C(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> •	7.9	-1.94	-2.17	0.23
21	(H <sub>2</sub> C=CH)(CH <sub>3</sub> )CHCH <sub>2</sub> •	8	-1.84	-2.13	0.29
22	Cyklopentenyl	7	-2.84	-2.62	-0.22
23	(H <sub>2</sub> C=CH)(CH <sub>3</sub> )CH•	7.49	-2.35	-2.32	-0.03
24	(H <sub>2</sub> C=CH) <sub>2</sub> CH•	7.25	-2.59	-2.54	-0.05
25	(H <sub>2</sub> C=CH)(C <sub>2</sub> H <sub>5</sub> )CH•	7.3	-2.54	-2.64	0.10
26	(CH <sub>3</sub> CH=CH)(CH <sub>3</sub> )CH•	7.07	-2.77	-2.44	-0.32
27	(H <sub>2</sub> C=CH)(CH <sub>3</sub> ) <sub>2</sub> C•	7.13	-2.71	-3.05	0.34
28	(CH <sub>3</sub> ) <sub>2</sub> (HCC)C•	7.44	-2.4	-2.4	0
29	C <sub>6</sub> H <sub>5</sub> •	8.32	-1.52	-1.52	0.00
30	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> •	7.24	-2.60	-2.59	-0.01
31	HOCH <sub>2</sub> •	7.56	-2.27	-2.33	0.05
32	(CH <sub>3</sub> )(HO)CH•	6.85	-2.99	-3.06	0.07
33	CH <sub>3</sub> OCH <sub>2</sub> •	6.9	-2.94	-2.70	-0.23
34	(CH <sub>3</sub> )(CH <sub>3</sub> O)CH•	6.5	-3.34	-3.44	0.10
35	HSCH <sub>2</sub> •	7.53	-2.30	-2.52	0.21
36	CH <sub>3</sub> SCH <sub>2</sub> •	6.85	-2.99	-2.77	-0.21
37	F <sub>3</sub> C•	8.76	-1.08	-1.26	0.18
38	F <sub>2</sub> HC•	8.78	-1.06	-1.05	-0.01
39	FH <sub>2</sub> C•	9.04	-0.8	-0.84	0.04
40	Cl <sub>3</sub> C•	8.06	-1.78	-1.84	0.06
41	Cl <sub>2</sub> HC•	8.32	-1.52	-1.44	-0.07
42	ClH <sub>2</sub> C•	8.75	-1.09	-1.03	-0.05
43	Br <sub>3</sub> C•	7.5	-2.34	-2.24	-0.09
44	Br <sub>2</sub> HC•	8.3	-1.54	-1.70	0.16
45	BrH <sub>2</sub> C•	8.61	-1.23	-1.17	-0.05
46	CH <sub>3</sub> CF <sub>2</sub> •	7.92	-1.92	-1.79	-0.12
47	CH <sub>3</sub> CHF•	7.93	-1.91	-1.57	-0.33
48	NCCH <sub>2</sub> •	9.9	0.06	0.06	0

<sup>a</sup> Regression statistics: multiple  $R$ , 0.9768;  $R^2$ , 0.9542; adjusted  $R^2$ , 0.9124; standard error, 0.2345; observations, 48.**Table 4.** Experimental Electron Affinities and Estimated Relative Electron Affinities of C-Centered Radicals<sup>a</sup>

no.	radical	EA <sup>14</sup> (eV)	EA - EA <sub>Me</sub> (eV)	(EA - EA <sub>Me</sub> ) <sub>est</sub> (eV)	residuals
1	H <sub>3</sub> C•	0.08	0.00	-0.03	0.03
2	CH <sub>3</sub> CH <sub>2</sub> •	-0.26	-0.34	-0.13	-0.21
3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> •	-0.07	-0.15	-0.17	0.02
4	(CH <sub>3</sub> ) <sub>2</sub> CH•	-0.32	-0.40	-0.24	-0.16
5	(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )CH•	-0.12	-0.20	-0.28	0.08
6	(CH <sub>3</sub> ) <sub>3</sub> C•	-0.16	-0.24	-0.34	0.11
7	H <sub>2</sub> C=CHCH <sub>2</sub> •	0.36	0.28	0.28	0.00
8	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> •	0.91	0.83	0.54	0.29
9	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH•	1.36	1.28	1.12	0.16
10	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C•	1.56	1.48	1.69	-0.21
11	F <sub>3</sub> C	1.84	1.76	1.68	0.08
12	F <sub>2</sub> HC•	1.21	1.13	1.11	0.02
13	FH <sub>2</sub> C•	0.20	0.12	0.54	-0.42
14	Cl <sub>3</sub> C•	2.17	2.09	2.15	-0.06
15	Cl <sub>2</sub> HC•	1.58	1.50	1.42	0.08
16	ClH <sub>2</sub> C•	0.80	0.72	0.70	0.02
17	Br <sub>3</sub> C•	1.73	1.65	1.71	-0.06
18	BrH <sub>2</sub> C•	0.82	0.74	0.55	0.19
19	CF <sub>3</sub> CF <sub>2</sub> •	1.81	1.73	1.68	0.05
20	CH <sub>3</sub> OCH <sub>2</sub> •	-0.02	-0.10	-0.10	0.00

<sup>a</sup> Regression statistics: multiple  $R$ , 0.9816;  $R^2$ , 0.9636; adjusted  $R^2$ , 0.8591; standard error, 0.1995; observations, 20.

For simplicity, the interatomic distances,  $r$ , were determined by using the Hyperchem software package allowing simple estimation of the standard geometries of the corresponding hydrocarbons. The accuracy of this procedure would probably be improved if optimized structures were used; however, this would make the approach more difficult and time-consuming and thereby less attractive.

This approach enabled us to check if, at the atomic level of additivity, there exists an overall operational characteristic parameter for a given atom. If it exists, the next question is to analyze its physical meaning.

In Tables 1 and 2, the results from the multiple regression analyses are presented. The operational atomic parameters,  $e_i$ , are denoted  $e^+$  and  $e^-$  for the ionization potentials and electron affinities, respectively.

The corresponding relative ionization potentials and electron affinities estimated from eq 15 using the operational atomic parameters,  $e^+$  and  $e^-$ , respectively, are given in Tables 3 and 4 along with the experimental numbers.

In Figures 1 and 2 the estimated relative ionization potentials and electron affinities, respectively, are plotted against the corresponding experimental values.

As can be seen from both Figures 1 and 2 and the regression statistics in Tables 3 and 4, the correlations between the experimental data and the values estimated from the overall atomic constants,  $e^+$  and  $e^-$ , are fairly good. Thus, the approach of atomic additivity seems to be valid also for thermochemical properties of radicals. Notably, the predicted ionization potential for the methyl radical deviates markedly from the corresponding experimental value. This is always a possible problem when using relative numerical approaches. Since we have chosen the methyl radical as reference ( $\Delta\text{IP} = 0$ ), the corresponding atomic  $e^+$  value for hydrogen should be zero (or very small) by definition. The resulting value for hydrogen is significantly lower than 0 ( $-0.25$ ), hence, the predicted relative ionization potential of the methyl radical is also far from zero. The same problem was observed by Taft when deriving an inductive scale using

**Table 5.** Operational Substituent Scales Derived from Ionization Potentials and Electron Affinities of C-Centered Radicals

no.	substituent	$\sigma_+^e$	$\sigma_-^e$	no.	substituent	$\sigma_+^e$	$\sigma_-^e$
1	H—	-0.21 ± 0.03	-0.008 ± 0.034	57	H <sub>3</sub> CSS—	-2.85 ± 0.25	
2	H <sub>3</sub> C—	-0.94 ± 0.15	-0.11 ± 0.16	58	<i>trans</i> -FCH=CH—	-1.2 ± 0.1	0.38 ± 0.24
3	(CH <sub>3</sub> ) <sub>2</sub> CH—	-1.6 ± 0.12	-0.20 ± 0.14	59	<i>trans</i> -ClCH=CH—	-1.26 ± 0.11	0.43 ± 0.24
4	(CH <sub>3</sub> ) <sub>3</sub> C—	-1.93 ± 0.14	-0.24 ± 0.17	60	<i>trans</i> -BrCH=CH—	-1.29 ± 0.11	0.41 ± 0.25
5	C <sub>2</sub> H <sub>5</sub> —	-1.27 ± 0.09	-0.16 ± 0.11	61	<i>cis</i> -FCH=CH—	-1.23 ± 0.11	0.44 ± 0.24
6	<i>n</i> -C <sub>4</sub> H <sub>9</sub> —	-1.50 ± 0.11	-0.18 ± 0.13	62	<i>cis</i> -ClCH=CH—	-1.34 ± 0.12	0.55 ± 0.11
7	<i>n</i> -C <sub>3</sub> H <sub>7</sub> —	-1.42 ± 0.11	0.17 ± 0.11	63	<i>cis</i> -BrCH=CH—	-1.42 ± 0.12	0.52 ± 0.26
8	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> —	-1.47 ± 0.12	-0.18 ± 0.14	64	-1-FC=CH <sub>2</sub>	-1.24 ± 0.11	0.47 ± 0.24
9	(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )CH—	-1.74 ± 0.13	-0.22 ± 0.15	65	-1-ClC=CH <sub>2</sub>	-1.35 ± 0.12	0.58 ± 0.11
10	HO—	-1.91 ± 0.14	-0.076 ± 0.23	66	-1-BrC=CH <sub>2</sub>	-1.42 ± 0.12	0.56 ± 0.26
11	H <sub>3</sub> CO—	-2.28 ± 0.17	-0.12 ± 0.26	67	F <sub>2</sub> C=CH—	-1.27 ± 0.11	0.51 ± 0.24
12	-CH <sub>2</sub> OH	-1.56 ± 0.16	-0.14 ± 0.20	68	Cl <sub>2</sub> C=CH—	-1.44 ± 0.12	0.68 ± 0.26
13	-CH <sub>2</sub> OCH <sub>3</sub>	-1.72 ± 0.17	-0.16 ± 0.22	69	Br <sub>2</sub> C=CH—	-1.55 ± 0.13	0.64 ± 0.27
14	-CN	0.48 ± 0.49		70	C <sub>6</sub> H <sub>5</sub> —	-1.46 ± 0.15	0.56 ± 0.07
15	-CH <sub>2</sub> CN	-0.53 ± 0.36		71	<i>p</i> -F-C <sub>6</sub> H <sub>4</sub> —	-1.47 ± 0.15	0.59 ± 0.07
16	-C <sub>2</sub> H <sub>4</sub> CN	-1.06 ± 0.21		72	<i>p</i> -Cl- C <sub>6</sub> H <sub>4</sub> —	-1.50 ± 0.15	0.62 ± 0.08
17	H <sub>2</sub> N—	-2.73 ± 0.14		73	<i>p</i> -Br- C <sub>6</sub> H <sub>4</sub> —	-1.52 ± 0.15	0.65 ± 0.08
18	H <sub>3</sub> CNH—	-2.37 ± 0.16		74	<i>m</i> -F- C <sub>6</sub> H <sub>4</sub> —	-1.46 ± 0.15	0.60 ± 0.07
19	(H <sub>3</sub> C) <sub>2</sub> N—	-3.68 ± 0.19		75	<i>m</i> -Cl- C <sub>6</sub> H <sub>4</sub> —	-1.49 ± 0.15	0.64 ± 0.08
20	H <sub>2</sub> NCH <sub>2</sub> —	-1.98 ± 0.17		76	<i>m</i> -Br- C <sub>6</sub> H <sub>4</sub> —	-1.52 ± 0.15	0.63 ± 0.08
21	CH <sub>3</sub> NHCH <sub>2</sub> —	-2.15 ± 0.18		77	<i>p</i> -H <sub>2</sub> C=CH- C <sub>6</sub> H <sub>4</sub> —	-1.56 ± 0.16	0.58 ± 0.09
22	(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> —	-2.32 ± 0.19		78	<i>m</i> -H <sub>2</sub> C=CH- C <sub>6</sub> H <sub>4</sub> —	-1.56 ± 0.16	0.59 ± 0.10
23	H <sub>2</sub> C=CH—	-1.16 ± 0.10	0.30 ± 0.24	79	<i>p</i> -F <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> —	-1.56 ± 0.16	0.63 ± 0.08
24	H <sub>2</sub> C=CHCH <sub>2</sub> —	-1.37 ± 0.16	0.003 ± 0.210	80	<i>p</i> -Cl <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> —	-1.63 ± 0.16	0.70 ± 0.09
25	H <sub>2</sub> C=CHCH(CH <sub>3</sub> )—	-1.70 ± 0.15	-0.039 ± 0.212	81	<i>p</i> -Br <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> —	-1.68 ± 0.16	0.75 ± 0.09
26	<i>cis</i> -H <sub>3</sub> CCH=CH—	-1.47 ± 0.12	0.27 ± 0.26	82	<i>p</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> —	-1.52 ± 0.15	0.55 ± 0.08
27	<i>trans</i> -H <sub>3</sub> CCH=CH—	-1.06 ± 0.11	0.28 ± 0.25	83	<i>m</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> —	-1.52 ± 0.15	0.55 ± 0.08
28	HCC—	-0.51 ± 0.24		84	F <sub>5</sub> C <sub>6</sub> —	-1.64 ± 0.17	0.94 ± 0.09
29	HCCCCH <sub>2</sub> —	-1.10 ± 0.21		85	Cl <sub>5</sub> C <sub>6</sub> —	-1.96 ± 0.19	0.26 ± 0.11
30	H <sub>3</sub> CCCCH <sub>2</sub> —	-1.20 ± 0.22		86	Br <sub>5</sub> C <sub>6</sub> —	-2.17 ± 0.20	1.18 ± 0.12
31	H <sub>3</sub> CCC—	-0.63 ± 0.25		87	<i>p</i> -H <sub>2</sub> N- C <sub>6</sub> H <sub>4</sub> —	-1.65 ± 0.16	
32	HS—	-2.1 ± 0.2		88	<i>m</i> -H <sub>2</sub> N- C <sub>6</sub> H <sub>4</sub> —	-1.70 ± 0.16	
33	H <sub>3</sub> CS—	-2.35 ± 0.20		89	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> N- C <sub>6</sub> H <sub>4</sub> —	-1.87 ± 0.18	
34	HSCH <sub>2</sub> —	-1.80 ± 0.19		90	<i>p</i> -H <sub>3</sub> CO- C <sub>6</sub> H <sub>4</sub> —	-1.63 ± 0.16	0.55 ± 0.09
35	H <sub>3</sub> CSCH <sub>2</sub> —	-1.92 ± 0.20		91	<i>m</i> -H <sub>3</sub> CO- C <sub>6</sub> H <sub>4</sub> —	-1.65 ± 0.16	0.57 ± 0.09
36	Cl—	-0.62 ± 0.06	0.72 ± 0.05	92	<i>p</i> -HS- C <sub>6</sub> H <sub>4</sub> —	-1.63 ± 0.16	
37	CCl <sub>3</sub> —	-1.57 ± 0.12	0.81 ± 0.13	93	<i>m</i> -HS- C <sub>6</sub> H <sub>4</sub> —	-1.67 ± 0.17	
38	CHCl <sub>2</sub> —	-1.36 ± 0.11	0.5 ± 0.11	94	<i>p</i> -H <sub>3</sub> CS- C <sub>6</sub> H <sub>4</sub> —	-1.69 ± 0.17	
39	CH <sub>2</sub> Cl—	-1.28 ± 0.09	0.19 ± 0.10	95	<i>m</i> -H <sub>3</sub> CS- C <sub>6</sub> H <sub>4</sub> —	-1.75 ± 0.17	
40	F—	-0.42 ± 0.05	0.56 ± 0.04	96	<i>p</i> -HO- C <sub>6</sub> H <sub>4</sub> —	-1.57 ± 0.15	0.56 ± 0.09
41	CF <sub>3</sub> —	-1.2 ± 0.1	0.42 ± 0.10	97	<i>m</i> -HO- C <sub>6</sub> H <sub>4</sub> —	-1.59 ± 0.16	0.57 ± 0.09
42	CHF <sub>2</sub> —	-1.12 ± 0.09	0.23 ± 0.10	98	C <sub>6</sub> H <sub>5</sub> -NH—	-3.52 ± 0.20	
43	CH <sub>2</sub> F—	-1.03 ± 0.08	0.043 ± 0.090	99	<i>p</i> -H <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -NH—	-3.68 ± 0.21	
44	Br—	-0.65 ± 0.06	0.57 ± 0.06	100	<i>p</i> -H <sub>2</sub> N- C <sub>6</sub> H <sub>4</sub> -N(CH <sub>3</sub> )—	-3.86 ± 0.23	
45	CBBr <sub>3</sub> —	-1.68 ± 0.13	0.67 ± 0.15	101	<i>p</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> -NH—	-3.58 ± 0.21	
46	CHBr <sub>2</sub> —	-1.43 ± 0.11	0.41 ± 0.13	102	C <sub>6</sub> H <sub>5</sub> -S—	-2.64 ± 0.25	
47	CH <sub>2</sub> Br—	-1.19 ± 0.09	0.15 ± 0.10	103	<i>p</i> -HS-C <sub>6</sub> H <sub>4</sub> -S—	-2.72 ± 0.26	
48	FCH <sub>2</sub> S—	-2.38 ± 0.21		104	<i>p</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> -S—	-2.69 ± 0.25	
49	ClCH <sub>2</sub> S—	-2.43 ± 0.21		105	C <sub>6</sub> H <sub>5</sub> -O—	-2.78 ± 0.23	0.27 ± 0.27
50	BrCH <sub>2</sub> S—	-2.46 ± 0.21		106	<i>p</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> -O—	-2.83 ± 0.23	0.27 ± 0.27
51	FCH <sub>2</sub> O—	-2.33 ± 0.17	-0.04 ± 0.26	107	<i>m</i> -H <sub>3</sub> C- C <sub>6</sub> H <sub>4</sub> -O—	-2.87 ± 0.24	0.26 ± 0.27
52	ClCH <sub>2</sub> O—	-2.38 ± 0.18	0.022 ± 0.26	108	<i>p</i> -H <sub>3</sub> CO- C <sub>6</sub> H <sub>4</sub> -O—	-2.92 ± 0.24	0.26 ± 0.28
53	BrCH <sub>2</sub> O—	-2.43 ± 0.18	0.0037 ± 0.2669	109	<i>p</i> -F- C <sub>6</sub> H <sub>4</sub> -O—	-2.79 ± 0.23	0.30 ± 0.27
54	HOO—	-2.54 ± 0.18	-0.1 ± 0.3	110	<i>p</i> -Cl- C <sub>6</sub> H <sub>4</sub> -O—	-2.81 ± 0.23	0.32 ± 0.27
55	H <sub>3</sub> COO—	-2.70 ± 0.20	-0.12 ± 0.31	111	<i>p</i> -Br- C <sub>6</sub> H <sub>4</sub> -O—	-2.83 ± 0.23	0.32 ± 0.27
56	HSS—	-2.75 ± 0.24					

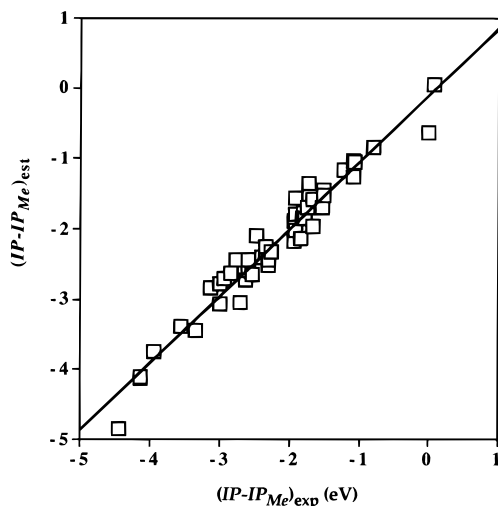
the methyl substituent as the zero-point.<sup>15</sup> Nevertheless, the relatively large deviation for the methyl radical does not affect the rather high quality of the main set of data. Note that, when using eq 15 to predict absolute ionization potentials, the experimental value for the methyl radical should be used.

Upon closer inspection of Table 3 we also note that the predictions for the simplest primary, secondary, and tertiary hydrocarbons (entries 2, 6, and 7) are somewhat less accurate than the predictions for the more complex hydrocarbons (entries 3, 4, 5, and 7). For entries 9–11 we also see that ring strain seems to affect the accuracy of the prediction. Another notable point is entry 16, (CH<sub>3</sub>)<sub>2</sub>(NH<sub>2</sub>)C•, which is

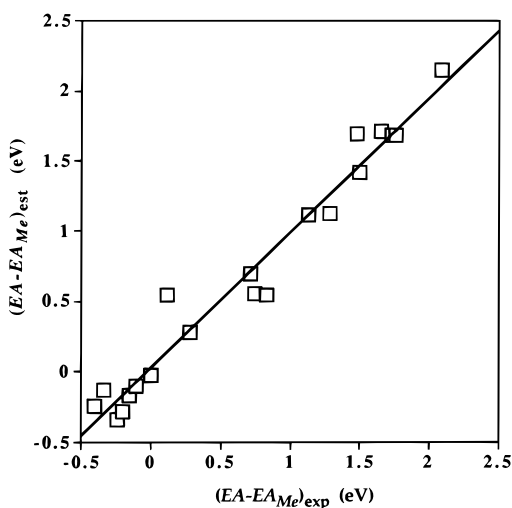
the only  $\alpha$ -amino substituted radical that deviates markedly from the corresponding experimental value. Interestingly, the points with the largest residuals ( $\geq 0.3$ ) all have methyl substituents in the  $\alpha$ -position. Two of these points have positive residuals, i.e., the predicted ionization potentials are lower than the corresponding experimental values, and five have negative residuals. A positive residual means that the total effect of substitution is less than additive which could imply stabilization of the radical, and, consequently, a negative residual could imply stabilization of the corresponding cation. The reason for this discrepancy is not obvious.

As can be seen in Tables 1 and 2, the operational atomic parameters with the largest uncertainty are N, O, C(sp),





**Figure 1.** Estimated relative ionization potentials of C-centered radicals plotted against the corresponding experimental values (see Table 3).



**Figure 2.** Estimated relative electron affinities of C-centered radicals plotted against the corresponding experimental values (see Table 4).

N(sp), and S for which resonance effects may play a significant role. This relatively large uncertainty indicates the presence of resonance effects or other effects that are not proportional to  $r^{-2}$ . Electron affinity data for CN- and NO<sub>2</sub>-substituted radicals are also available (NCCH<sub>2</sub>•, NO<sub>2</sub>-CH<sub>2</sub>•, and (NO<sub>2</sub>)<sub>3</sub>C•), but they were not included in the numerical treatment. The reason for this is that NCCH<sub>2</sub>• contains two atoms for which the operational parameters are unknown; therefore, numerical treatment would be pointless, and it is also obvious that the contributions from several NO<sub>2</sub>-groups at the α-carbon are not additive. Admittedly, for strongly electron-withdrawing substituents, the additive approach does not seem to be useful.

Analysis of the physical meaning of the  $e_i$ -parameters is not straightforward. However, a physical interpretation of these findings is under way.

A more useful tool for prediction of redox properties of C-centered radicals would of course be additive substituent constants rather than the additive operational atomic parameters which also require data on interatomic distances. In general, constants for substituents containing atoms from Tables 1 and 2 can be calculated from eq 15. Using this

approach we can also calculate substituent constants for different conformers. For simplicity and clarity, we have calculated the corresponding substituent constants for some of the most commonly occurring organic substituents. These two new substituent scales (denoted  $\sigma_+^e$  and  $\sigma_-^e$ , respectively) are presented in Table 5.

To predict the redox properties of C-centered radicals using these new substituent scales, eq 16 should be used

$$\text{IP(EA)} = \text{IP}_0(\text{EA}_0) + \sum \sigma_+^e(\sigma_-^e) \quad (16)$$

where IP<sub>0</sub> and EA<sub>0</sub> are the ionization potential and electron affinity, respectively, of the methyl radical (9.84 and 0.08 eV). Taking solvation into account, eq 16 could also be used to predict one-electron oxidation and reduction potentials in solution (eq 17).

$$E^\circ = \text{IP(EA)} - 4.44 - \frac{\Delta G_{\text{solv}}^\circ(\text{R}^+(\text{R}^-)) - \Delta G_{\text{solv}}^\circ(\text{R}^+(\text{R}^\bullet))}{F} \quad (17)$$

The term 4.44 (±0.02) eV is the absolute potential of the hydrogen electrode in water,  $\Delta G_{\text{solv}}^\circ$  is the free energy of solvation, and  $F$  is the Faraday constant. The use of this relationship requires data on differences in free energy of solvation of the radical and the corresponding cation or anion. In this case, reliable linear solvation energy relationships for organic ions would be greatly appreciated.

## CONCLUSIONS

In this paper we have shown that substituent effects on both ionization potentials and electron affinities of C-centered radicals can be described in terms of additive atomic contributions (except for strongly electron-withdrawing substituents). The physical meaning of these parameters is yet to be determined. Based on these operational atomic parameters, additive substituent constants have also been derived.

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