Substituent Effects on Thermochemical Properties of C-, N-, O-, and S-Centered Radicals. Physical Interpretation of Substituent Effects

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Substituent effects on ionization potentials and electron affinities of C-, N-, O-, and S-centered radicals were analyzed in terms of additive operational atomic contributions. The physical factors governing the estimated operational atomic parameters were analyzed in terms of fundamental atomic properties. The operational atomic parameters were found to depend on the electronegativity and the covalent radius which for each type of radical is described quantitatively by two separate sets of equations for ionization potentials and electron affinities, respectively.

INTRODUCTION

Substituent effects in radical chemistry is a topic of long standing. Quantitative relationships between structure and property or reactivity have been found for a large number of radical systems. Most of these relationships describe effects of ring substituents on aromatic radicals.

Previous studies of ionization potentials of different classes of closed-shell compounds have resulted in quantitative correlations between ionization potentials and inductive, steric, and resonance properties of substituents.[2] In a recent paper we derived an empirical additive approach to calculate ionization potentials (IP) and electron affinities (EA) of carbon-centered radicals from empirical atomic parameters (denoted e^+ and e^-, respectively).[3] These atomic parameters describe overall additive contributions of atoms of a certain type to the relative values of ionization potentials and electron affinities:

$$\mathrm{IP}_{\mathrm{R}_n\mathrm{X}\bullet} - \mathrm{IP}_{\mathrm{H}_n\mathrm{X}\bullet} = \sum_{i\subset R} \frac{e_i^+}{r_i^2} \tag{1}$$

$$\mathrm{EA}_{\mathrm{R}_n\mathrm{X}\bullet} - \mathrm{EA}_{\mathrm{H}_n\mathrm{X}\bullet} = \sum_{i\subset R} \frac{e_i^-}{r_i^2} \tag{2}$$

where $\mathrm{IP}_{\mathrm{H}_n\mathrm{X}\bullet}/\mathrm{EA}_{\mathrm{H}_n\mathrm{X}\bullet}$ correspond to the ionization potential/electron affinity of the methyl radical which was chosen as the standard in this case and r_i is the direct distance from the ith atom of a substituent to the carbon−radical center. The atomic parameters were obtained using multiparametric regression analysis of experimental data in accordance with eq 1 and 2. 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 radical structures were used; however, this would make the approach more difficult and time-consuming and thereby less attractive.

Although the parameters e^- and e^+ allow us to predict the ionization potential and electron affinity of C-centered radicals with reasonable accuracy, the physical meaning of these parameters is unclear. Furthermore, the approach is not universal since we can only predict ionization potentials and electron affinities for radicals, constituted by atoms included in the original multiregression analysis. To increase the generality of this method, we need to understand the fundamental physical meaning of the operational atomic parameters (e^- and e^+) so that they can be determined from fundamental properties of any atom.

In this work, we have studied substituent effects on the gas-phase redox properties of N-, O-, and S-centered radicals. From these results and the previously published results on C-centered radicals we have made an attempt to establish the factors determining the operational atomic parameters, i.e., to clarify the physical meaning of these constants.

THEORY

To establish the factors determining the operational atomic parameters, we have used two previously published models for steric[5] and inductive[6] substituent effects. Briefly, the steric effect of a substituent attached to a given reaction center has been described simply as mechanical shielding of the reaction center by the atoms of the substituent:

$$R'_{\mathrm{S}} = \sum_{i=1}^{n} \frac{R_i^2}{4r_i^2} \tag{3}$$

where n is the number of substituent atoms, R_i is the covalent radius of the ith atom, r_i is the direct distance from the ith atom to the reaction center, and R'_{S} reflects the specific surface of the reaction center screened by the atoms of the substituents.

Inductive interaction of substituents with the reaction center has also been interpreted in terms of additive summation of atomic contributions to the overall interaction:

$$\sigma^* = \sum_{i=1}^{n} \frac{\sigma_{\mathrm{A}_i}}{r_i^2} \tag{4}$$

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where σ_A is an overall empirical atomic value, depending on the chemical nature and valence state of the substituting atom and on the nature of the reaction center. There is a correlation between the overall empirical atomic values, σ_A, and the difference in electronegativity of the *i*th atom and the reaction center, $\Delta\chi_{i-RC}$, and the squared covalent radius.

$$\sigma_A = 7.84\Delta\chi_{i-RC}R_i^2 \tag{5}$$

Thus, eq 5 clarifies the physical meaning of the empirical σ_A constants and allows for determination of inductive substituent constants from fundamental atomic properties:

$$\sigma^* = \sum_{i=1}^{n} \frac{\sigma_{A_i}}{r_i^2} = 7.84 \sum_{i=1}^{n} \frac{\Delta\chi_{i-RC}R_i^2}{r_i^2} \tag{6}$$

By using eq 5, a new scale of inductive electronegativities of purely empirical nature has been defined.[6,7] This scale is correlated to Pauling's electronegativity scale and to some other scales with the notable exception of the value for carbon. The electronegativity of carbon according to this new scale is 2.1, which was argued to be a more reasonable value than Pauling's 2.55 based on the reactivity.[6] Furthermore, Pauling's value implies that carbon would be more electron withdrawing than for instance phosphorus ($\chi = 2.2$) and iodine ($\chi = 2.4$), which is clearly not the case. The low polarity of C−H bonds would also imply that $\chi = 2.55$ is too high a value for carbon.

The estimated atomic parameters, e^+ and e^-, could contain steric, inductive, and resonance contributions. By definition, the atomic parameters derived in ref 3 and in this work are proportional to $\sum 1/r^2$. Thus, if included in the operational atomic parameters, the corresponding resonance contribution should be proportional to the atomic σ_A constant or be negligible. We do, however, not find any reason to believe that the resonance contribution should be proportional to $\sum 1/r^2$. To separate the inductive and steric contributions properly, we would need the inductive electronegativity for the radical centers. Unfortunately, these values are not available but instead of trying to find correlations between e^+/e^- and $\Delta\chi R^2$ and R^2, according to eqs 3 and 6, we have tried to find correlations between e^+/e^- and χR^2 and R^2.

$$e_i^+/e_i^- = A\chi_i R_i^2 + BR_i^2 \tag{7}$$

The term *B* may then contain the inductive electronegativity for the radical atom and a constant describing the pure sterical contribution (if any); thus, eq 7 describes both the inductive and steric contribution as described by eqs 3 and 6. However, we will not be able to separate these two terms.

RESULTS AND DISCUSSION

Using the approach previously described for C-centered radicals, i.e., by multiparametric regression analysis of experimental data in accordance with eqs 1 and 2, we analyzed the substituent effects on ionization potentials and electron affinities of N-, O-, and S-centered radicals. Statistics for the empirical correlations are given in Table 1, and the ionization potentials and electron affinities estimated from these correlations are presented in Tables 2 and 3 along with the corresponding experimental values. The resulting operational atomic parameters, e^+/e^-, are given in Tables 4 and 5 along with the inductive electronegativities, χ_i, and the squared covalent radius, R_i^2.

Table 1. Statistical Parameters of Correlations 1 and 2 for Different Types of Free Radicals

type of radical	property	no. of observations	*R*	*F*	*S* (eV)
C-centered	IP	48	0.98	62.5	0.23
	EA	20	0.98	39.8	0.20
N-centered	IP	5	0.97	3.7	1.0
	EA	6	0.97	18.8	0.22
O-centered	IP	10	0.99	20.0	0.36
	EA	12	0.98	14.9	0.12
S-centered	IP	7	0.93	2.5	0.61
	EA	10	0.84	3.1	0.15

As can be seen in Table 1, the quality of the correlations is fairly good with the exception of the electron affinities for S-centered radicals. For all sets of data except the C-centered radicals, the number of data is relatively sparse. Nevertheless, the fact that we obtain correlations for other types of radicals than the previously studied C-centered radicals indicates that this relatively simple approach is more general than first assumed.

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

Data Obtained from Ionization Potentials. The parameters for the correlations for the C-, N-, O-, and S-centered radicals, analyzed in terms of eq 7, are given in Table 6. In the case of C-centered radicals, N, O, and S were omitted from the linear regression for reasons that will be discussed later.

Equation 7 can also be written as eq 8 where *C* is *B*/*A*. For clarity, values for *C* are also given in Table 6. As can

$$e_i^+/e_i^- = A(\chi_i + C)R_i^2 \tag{8}$$

readily be seen from Table 6 and eq 8, the contribution from most possible substituent atoms is a lowering of the ionization potential compared to that of the unsubstituted reference radical. Only for atoms with extremely high inductive electronegativity values (e.g. N_{sp}, $\chi = 6.76$)[6,7] we can expect an increased ionization potential.

The deviation of the atomic parameters of N, O, and S from the general correlations could be due to resonance effects which cannot be described in terms of the fundamental atomic properties and interatomic distances used here. These deviations will be discussed in more detail later.

In Table 4, the atomic parameters e^+ calculated from eq 7 are given. The resulting ionization potentials are presented in Table 2.

As can be seen in Table 2, 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 ($\Delta IP = 0$), 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; hence, the predicted relative ionization potential of the methyl radical is also far from zero. The same problem was observed by Taft when

Table 2. Experimental, Estimated (from Equation 1), and Calculated (from Equation 7) Ionization Potentials, IP, of C-, N-, O-, and S-Centered Radicals

no.	radical	IP_{expt}[4] (eV)	IP_{est} (eV)	$\Delta IP_{expt-est}$ (eV)	IP_{calc} (eV)	$\Delta IP_{expt-calc}$ (eV)
1	$H_3C^{\bullet}$	9.84	9.21	0.63	9.11	0.73
2	$CH_3CH_2^{\bullet}$	8.12	8.47	−0.36	8.37	−0.25
3	$C_2H_5CH_2^{\bullet}$	8.09	8.14	−0.05	8.03	0.06
4	$C_3H_7CH_2^{\bullet}$	8.02	8	0.02	7.88	0.14
5	$(CH_3)_2CHCH_2^{\bullet}$	7.93	7.81	0.12	7.68	0.25
6	$(CH_3)_2CH^{\bullet}$	7.37	7.74	−0.37	7.62	−0.25
7	$(CH_3)(C_2H_5)CH^{\bullet}$	7.25	7.41	−0.16	7.28	−0.03
8	$(CH_3)_3C^{\bullet}$	6.7	7	−0.3	6.88	−0.18
9	cyclo-$C_3H_5^{\bullet}$	8.18	7.87	0.31	7.77	0.41
10	cyclo-$C_4H_7^{\bullet}$	7.54	7.41	0.13	7.29	0.25
11	cyclo-$C_5H_9^{\bullet}$	7.21	7.11	0.1	6.98	0.23
12	$H_2NCH_2^{\bullet}$	6.29	6.45	−0.16	8.6	−2.31
13	$CH_3NHCH_2^{\bullet}$	5.9	6.1	−0.20	8.23	−2.33
14	$(CH_3)_2NCH_2^{\bullet}$	5.7	5.74	−0.04	7.86	−2.16
15	$CH_3(NH_2)CH^{\bullet}$	5.7	5.72	−0.02	7.86	−2.16
16	$(CH_3)_2(NH_2)C^{\bullet}$	5.4	4.98	0.42	7.11	−1.71
17	$H_2C{=}CHCH_2^{\bullet}$	8.18	8.25	−0.07	8.42	−0.24
18	$(CH_2{=}C)(CH_3)CH_2^{\bullet}$	7.9	7.95	−0.05	8.11	−0.21
19	$H_2C{=}CHCH_2CH_2^{\bullet}$	8.04	8.05	−0.01	8.04	0
20	$H_2C{=}C(C_2H_5)CH_2^{\bullet}$	7.9	7.66	0.24	7.81	0.09
21	$(H_2C{=}CH)(CH_3)CHCH_2^{\bullet}$	8	7.71	0.29	7.69	0.31
22	cyclopentenyl	7	7.22	−0.22	7.38	−0.38
23	$(H_2C{=}CH)(CH_3)CH^{\bullet}$	7.49	7.52	−0.03	7.67	−0.18
24	$(H_2C{=}CH)_2CH^{\bullet}$	7.25	7.3	−0.05	7.73	−0.48
25	$(H_2C{=}CH)(C_2H_5)CH^{\bullet}$	7.3	7.19	0.11	7.33	−0.03
26	$(CH_3CH{=}CH)(CH_3)CH^{\bullet}$	7.07	7.39	−0.32	7.54	−0.47
27	$(H_2C{=}CH)(CH_3)_2C^{\bullet}$	7.13	6.78	0.35	6.93	0.2
28	$(CH_3)_2(HCC)C^{\bullet}$	7.44	7.44	0	7.51	−0.07
29	$C_6H_5^{\bullet}$	8.32	8.31	0.01	8.46	−0.14
30	$C_6H_5CH_2^{\bullet}$	7.24	7.24	−0.01	7.42	−0.19
31	$HOCH_2^{\bullet}$	7.56	7.51	0.05	8.82	−1.25
32	$(CH_3)(HO)CH^{\bullet}$	6.85	6.77	0.08	8.07	−1.22
33	$CH_3OCH_2^{\bullet}$	6.9	7.13	−0.23	8.43	−1.53
34	$(CH_3)(CH_3O)CH^{\bullet}$	6.5	6.4	0.1	7.68	−1.18
35	$HSCH_2^{\bullet}$	7.54	7.32	0.22	8.44	−0.91
36	$CH_3SCH_2^{\bullet}$	6.85	7.07	−0.22	8.19	−1.34
37	$F_3C^{\bullet}$	8.76	8.57	0.19	9.03	−0.27
38	$F_2HC^{\bullet}$	8.78	8.79	−0.01	9.06	−0.28
39	$FH_2C^{\bullet}$	9.04	9	0.04	9.08	−0.04
40	$Cl_3C^{\bullet}$	8.06	7.99	0.07	7.82	0.24
41	$Cl_2HC^{\bullet}$	8.32	8.4	−0.08	8.25	0.07
42	$ClH_2C^{\bullet}$	8.75	8.8	−0.05	8.68	0.07
43	$Br_3C^{\bullet}$	7.5	7.59	−0.09	7.42	0.08
44	$Br_2HC^{\bullet}$	8.3	8.13	0.17	7.99	0.31
45	$BrH_2C^{\bullet}$	8.61	8.67	−0.06	8.55	0.06
46	$CH_3CF_2^{\bullet}$	7.92	8.05	−0.13	8.31	−0.39
47	$CH_3CHF^{\bullet}$	7.93	8.26	−0.33	8.34	−0.41
48	$NCCH_2^{\bullet}$	9.9	9.9	0	9.18	0.72
49	$H_2N^{\bullet}$ (ref)	10.78	10.36	0.43	9.08	1.70
50	$CH_3NH^{\bullet}$	6.7	7.55	−0.85	6.7	0
51	$(CH_3)_2N^{\bullet}$	5.17	4.75	0.43	4.32	0.85
52	$C_6H_5NH^{\bullet}$	8.26	8.26	0	4.82	3.44
53	$H_2N{-}NH^{\bullet}$	7.61	7.61	0	7.39	0.22
54	$HO^{\bullet}$ (ref)	13.017	13.04	−0.02	11.99	1.02
55	$HOO^{\bullet}$	11.35	11.35	0	11.45	−0.10
56	$FO^{\bullet}$	12.78	12.78	0	12.38	0.40
57	$ClO^{\bullet}$	10.885	10.89	0	10.84	0.05
58	$BrO^{\bullet}$	10.46	10.46	0	10.4	0.06
59	$IO^{\bullet}$	9.66	9.66	0	9.8	−0.14
60	$CH_3O^{\bullet}$	10.72	10.39	0.33	9.31	1.41
61	$C_2H_5O^{\bullet}$	9.11	9.47	−0.36	8.13	0.98
62	$C_3H_7O^{\bullet}$	9.2	9.1	0.11	7.62	1.58
63	$C_6H_5O^{\bullet}$	8.56	8.56	0	8.14	0.42
64	$HS^{\bullet}$ (ref)	10.429	10.43	0	10.04	0.39
65	$FS^{\bullet}$	10.16	10.16	0	9.81	0.35
66	$CH_3S^{\bullet}$	9.262	9.38	−0.12	8.64	0.62
67	$C_2H_5S^{\bullet}$	9.6	8.92	0.68	7.93	1.67
68	$C_3H_7S^{\bullet}$	8.2	8.73	−0.53	7.61	0.59
69	$C_6H_5S^{\bullet}$	8.63	8.63	0	7.82	0.81
70	$CH_3SS^{\bullet}$	8	8	0	8.05	−0.05

deriving an inductive scale using the methyl substituent as the zero point.[8] In the present case however, there could also be other reasons for this discrepancy, which will be discussed later.

Table 3. Experimental, Estimated (from Equation 2), and Calculated (from Equation 7) Electron Affinities, EA, of C-, N-, O-, and S-Centered Radicals

no.	radical	EA_{exp}[4] (eV)	EA_{est} (eV)	$\Delta EA_{expt-est}$ (eV)	EA_{calc} (eV)	$\Delta EA_{exp-calc}$ (eV)
1	$H_3C^\bullet$	0.08	0.05	0.03	0.14	−0.06
2	$CH_3CH_2^\bullet$	−0.26	−0.05	−0.21	0.21	−0.47
3	$CH_3CH_2CH_2^\bullet$	−0.07	−0.09	0.02	0.24	−0.31
4	$(CH_3)_2CH^\bullet$	−0.32	−0.16	−0.16	0.27	−0.59
5	$(CH_3)(C_2H_5)CH^\bullet$	−0.12	−0.2	0.08	0.30	−0.42
6	$(CH_3)_3C^\bullet$	−0.16	−0.27	0.11	0.34	−0.50
7	$H_2C{=}CHCH_2^\bullet$	0.36	0.36	0.00	0.27	0.09
8	$C_6H_5CH_2^\bullet$	0.91	0.62	0.29	0.49	0.42
9	$(C_6H_5)_2CH^\bullet$	1.36	1.2	0.16	0.84	0.52
10	$(C_6H_5)_3C^\bullet$	1.56	1.77	−0.21	1.19	0.37
11	F_3C	1.84	1.76	0.08	2.27	−0.43
12	$F_2HC^\bullet$	1.21	1.19	0.02	1.56	−0.35
13	$FH_2C^\bullet$	0.20	0.62	−0.42	0.85	−0.65
14	$Cl_3C^\bullet$	2.17	2.23	−0.06	1.89	0.28
15	$Cl_2HC^\bullet$	1.58	1.5	0.08	1.31	0.27
16	$ClH_2C^\bullet$	0.80	0.78	0.02	0.73	0.07
17	$Br_3C^\bullet$	1.73	1.79	−0.06	1.91	−0.18
18	$BrH_2C^\bullet$	0.82	0.63	0.19	0.73	0.09
19	$CF_3CF_2^\bullet$	1.81	1.76	0.05	2.26	−0.45
20	$CH_3OCH_2^\bullet$	-0.02	−0.02	0.00	0.52	−0.54
21	$H_2N^\bullet$ (ref)	0.78	0.77	0.01	0.66	0.12
22	$CH_3NH^\bullet$	0.45	0.60	−0.15	0.50	−0.05
23	$(CH_3)_2N^\bullet$	0.38	0.43	−0.05	0.34	0.04
24	$C_6H_5NH^\bullet$	1.70	1.57	0.13	1.48	0.22
25	$C_6H_5(CH_3)N^\bullet$	1.65	1.40	0.25	1.32	0.33
26	$(C_6H_5)_2N^\bullet$	2.18	2.37	−0.19	2.30	−0.12
27	$HO^\bullet$ (ref)	1.83	1.83	0.00	1.86	−0.03
28	$HOO^\bullet$	1.08	1.08	0.00	2.14	−1.06
29	$FO^\bullet$	2.27	2.27	0.00	2.34	−0.06
30	$ClO^\bullet$	2.28	2.28	0.00	2.34	−0.07
31	$BrO^\bullet$	2.35	2.35	0.00	2.35	0.00
32	$IO^\bullet$	2.38	2.38	0.00	2.33	0.05
33	$CH_3O^\bullet$	1.62	1.62	0.00	1.94	−0.32
34	$C_2H_5O^\bullet$	1.72	1.72	0.00	1.98	−0.26
35	$C_3H_7O^\bullet$	1.79	1.79	0.00	1.99	−0.20
36	i-$C_3H_7O^\bullet$	1.84	1.84	0.00	2.01	−0.17
37	t-$C_4H_9O^\bullet$	1.9	11.91	0.00	1.96	−0.05
38	$C_6H_5O^\bullet$	2.25	2.25	0.00	2.21	0.04
39	$HS^\bullet$ (ref)	2.31	2.25	0.07	2.32	0.00
40	$CH_3SS^\bullet$	1.75	1.80	−0.05	1.81	−0.06
41	$CH_3S^\bullet$	1.87	2.12	−0.25	2.31	−0.45
42	$C_2H_5S^\bullet$	1.95	2.05	−0.10	2.31	−0.36
43	$C_3H_7S^\bullet$	2.00	2.02	−0.02	2.31	−0.32
44	i-$C_3H_7S^\bullet$	2.02	1.98	0.04	2.31	−0.30
45	t-$C_4H_9S^\bullet$	2.07	1.90	0.16	2.31	−0.24
46	$C_6H_5S^\bullet$	2.26	2.26	0.00	1.93	0.32
47	$HSS^\bullet$	1.90	1.86	0.05	1.81	0.09
48	$HOS^\bullet$	1.65	1.65	0.00	1.87	−0.22

Data Obtained from Electron Affinities. The parameters for the correlations for the C-, N-, O-, and S-centered radicals are given in Table 6. In Table 5, the atomic parameters e^-, calculated from eq 7 are given. The resulting electron affinities are given in Table 3.

PHYSICAL INTERPRETATION OF SUBSTITUENT EFFECTS

It is important to keep in mind that the ionization potentials and electron affinities of radicals are actually the enthalpy differences between a radical and the corresponding cation in the first case and between the anion and the radical in the latter case. Consequently, the effects described by eq 7 are combined by effects on both the radical and the corresponding ion. Positive $e^{+/-}$ values imply that the substituent atom stabilizes the radical more than the cation compared to the reference substance $H_nX^\bullet/H_nX^+$ in the case of ionization potentials and that the substituent atom stabilizes the anion more than the radical compared to $H_nX^-/H_nX^\bullet$ in the case of electron affinities. Negative $e^{+/-}$ values imply the opposite situation. Note that the term "stabilization" is arbitrary, and what we have referred to as stabilized could as well be referred to as less destabilized. This is analogous to the discussion about substituent effects on bond dissociation enthalpies where the observed effects can be attributed to both the molecule, R−X, and the radical, $R^\bullet$.[9,10]

As can be seen from the parameters presented in Table 6, a considerably high electronegativity is required for a substituent atom in order to stabilize the radical more than the corresponding cation. It is also obvious that most substituent atoms will stabilize the anion more than the corresponding radical, since a considerably low electronegativity would be required for the latter to occur. Judging from this, the main effects can be attributed to the ionic species.

Some information about the steric effects on ionization potentials can be obtained by comparing the adiabatic

Table 4. Operational Atomic Parameters e^{+}_{expt} Derived from Experimental Data and Theoretical Parameters e^{+}_{calc}, Calculated from Equation 7

radical	atom	χ_i	R_2	e^{+}_{expt}	e^{+}_{calc}	$e^{+}_{calc} - e^{+}_{calc}$
C•	H	2.10	0.090	−0.25 ± 0.04	−0.29	0.04
	C	2.10	0.593	−1.86 ± 0.11	−1.90	0.04
	C (sp^2)	2.25	0.449	−1.78 ± 0.14	−1.37	−0.41
	C (sp)	2.65	0.390	−0.80 ± 0.39	−0.55	−0.25
	C (ar)	2.45	0.449	−1.45 ± 0.14	−1.27	−0.18
	F	3.93	0.409	−0.78 ± 0.10	−0.50	−0.28
	Cl	3.09	0.980	−1.91 ± 0.19	−2.09	0.18
	Br	2.97	1.299	−2.73 ± 0.23	−2.94	0.21
	N	2.56	0.490	−6.15 ± 0.26	−1.33	−4.82
	O	3.05	0.436	−3.77 ± 0.27	−0.95	−2.82
	S	2.67	1.082	−6.61 ± 0.58	−2.78	−3.83
	N (sp)	6.76	0.3025	5.89	0.56	5.33
N•	H	2.10	0.090	−0.217 ± 0.485	−0.87	0.65
	C	2.10	0.593	−6.202 ± 1.361	−5.70	−0.50
	C (ar)	2.45	0.449	−1.934 ± 1.088	−4.14	2.21
	N	2.56	0.490	−5.996 ± 2.652	−4.46	−1.54
O•	H	2.10	0.090	0.022 ± 0.327	−0.94	0.96
	C	2.10	0.593	−5.407 ± 0.534	−6.22	0.81
	F	3.93	0.410	−0.498 ± 0.748	−1.34	0.84
	Cl	3.09	0.980	−6.307 ± 1.052	−6.45	0.14
	Br	2.97	1.300	−8.942 ± 1.244	−9.17	0.23
	I	2.80	1.769	−14.25 ± 1.51	−13.66	−0.59
	C (ar)	2.45	0.449	−4.071 ± 0.348	−4.09	0.02
	O	3.05	0.436	−3.663 ± 0.799	−2.93	−0.73
S•	H	2.10	0.090	0.003 ± 1.089	−0.69	0.69
	C	2.10	0.593	−3.370 ± 1.831	−4.57	1.2
	F	3.93	0.410	−0.814 ± 1.848	−1.88	1.07
	C (ar)	2.45	0.449	−2.429 ± 0.972	−3.19	0.76
	S	2.67	1.082	−8.680 ± 2.598	−7.25	−1.43

ionization potentials used here with the corresponding vertical ionization potentials. The adiabatic potential is the enthalpy difference between the radical and the cation where both structures are fully relaxed and the vertical potential is the enthalpy difference where the cation structure is identical to that of the radical. Consequently, the difference between the adiabatic and the vertical value corresponds to the structural reorganization connected with oxidation of the radical which is where steric effects should be of major significance. For the methyl radical, $CH_3^{\bullet}$, the adiabatic potential is identical

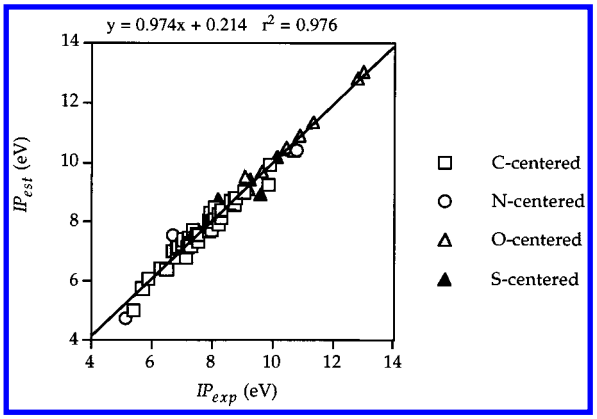

Figure 1. Estimated ionization potentials plotted against the corresponding experimental values for C- (squares), N- (circles), O- (open triangles), and S-centered radicals (filled triangles).

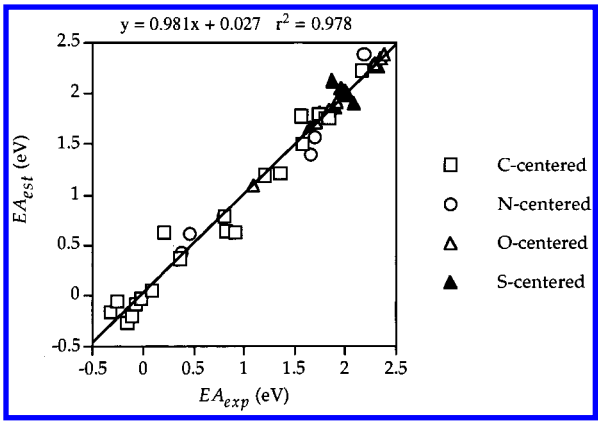

Figure 2. Estimated electron affinities plotted against the corresponding experimental values for C- (squares), N- (circles), O- (open triangles), and S-centered radicals (filled triangles).

to the vertical potential, which is rationalized by the fact that both the radical and the cation are planar. For other primary, secondary, and tertiary C-centered radicals, the radical center is not planar, while the cation is. Interestingly, the difference between the adiabatic potential and the vertical

Table 5. Operational Atomic Parameters e^{-}_{expt} Derived from Experimental Data and Theoretical Parameters e^{-}_{calc}, Calculated from Equation 7

radical center	atom	χ_i	R^2	e^{-}_{expt}	e^{-}_{calc}	$e^{-}_{expt} - e^{-}_{tcalc}$
C•	H	2.10	0.090	−0.01 ± 0.04	0.03	−0.04
	C	2.10	0.593	−0.26 ± 0.14	0.17	−0.43
	C (sp^2)	2.25	0.449	0.51 ± 0.37	0.24	0.27
	C (ar)	2.45	0.449	0.60 ± 0.06	0.38	0.22
	F	3.93	0.409	1.04 ± 0.08	1.35	−0.31
	Cl	3.09	0.980	2.22 ± 0.17	1.87	0.35
	Br	2.97	1.299	2.08 ± 0.23	2.22	−0.14
	O	3.05	0.436	−0.16 ± 0.44	0.80	−0.96
N•	H	2.10	0.090	−0.008 ± 0.093	−0.059	0.05
	C	2.10	0.593	−0.396 ± 0.255	−0.39	−0.01
	C (ar)	2.45	0.449	0.687 ± 0.091	0.69	0
O•	H	2.10	0.090	0.025 ± 0.098	0.029	0
	C	2.10	0.593	−0.104 ± 0.155	0.19	−0.29
	F	3.93	0.410	0.936 ± 0.242	1.07	−0.13
	Cl	3.09	0.980	1.328 ± 0.340	1.527	−0.20
	Br	2.97	1.300	1.839 ± 0.402	1.83	0.01
	I	2.80	1.769	2.338 ± 0.488	2.11	0.23
	C (ar)	2.45	0.449	0.379 ± 0.111	0.34	0.04
	O	3.05	0.436	−1.654 ± 0.257	0.66	−2.31
S•	H	2.10	0.090	−0.12 ± 0.261	−0.001	−0.12
	C	2.10	0.593	−0.41 ± 0.386	−0.008	−0.40
	C (ar)	2.45	0.449	−0.02 ± 0.236	−0.52	0.50
	O	3.05	0.436	−1.95 ± 0.482	−1.36	−0.60
	S	2.67	1.082	−1.84 ± 0.457	−2.09	0.26

Table 6. Statistical Parameters of the Correlations 7 for Different Types of Free Radicals

type of radical	param	A	B	$C = B/A$	N	R	F	S (eV)
C•	e^+	1.09 ± 0.33	−5.49 ± 0.97	−5.04	8[a]	0.95	28.3	0.27
	e^-	1.64 ± 0.43	−3.17 ± 1.26	−1.93	7[b]	0.95	23.25	0.33
N•	e^+	1.14 ± 10.7	−12.01 ± 24.9	−10.55	4	0.84	2.4	1.99
	e^-	6.24 ± 0.41	−13.76 ± 0.92	−2.20	3	0.998	111.8	1.04
O•	e^+	3.94 ± 1.01	−18.77 ± 2.93	−4.76	8	0.99	136.0	0.73
	e^-	1.25 ± 0.27	−2.31 ± 0.79	−1.84	7[b]	0.98	63.5	0.20
S•	e^+	1.71 ± 2.19	−11.29 ± 5.93	−6.61	5	0.94	10.8	1.38
	e^-	−3.27 ± 1.41	6.85 ± 3.68	−2.09	5	0.87	3.1	0.53

[a] Substituents containing O, N, S and N (sp) excluded. [b] Substituents containing O excluded.

potential is more or less constant (0.3−0.4 eV) for simple alkyl radicals.[4] The fact that the reorganization energy does not vary dramatically between primary, secondary, and tertiary radicals implies that there is no significant steric contribution to the adiabatic ionization potential but a constant reorganization energy contribution. The notable absence of this reorganization energy in the methyl case could also be the major reason for the large deviation in the predicted ionization potential for the methyl radical. For the other types of radicals, the discrepancy between the experimental ionization potential of the reference radical and the corresponding values estimated from the linear regression is small, but the values calculated from eq 7 deviate markedly from the experimental values. It should be pointed out that since the number of data for N-, O-, and S-centered radicals is rather limited, the correlations are very sensitive to errors in individual points. Consequently, we should avoid over-interpretation of these correlations.

On the basis of the above discussion, we can assume that the steric effect on ionization potentials and electron affinities is negligible and we can treat the substituent effects as purely inductive. In general, cations should be stabilized by electron donating substituents and anions should be stabilized by electron withdrawing substituents. According to eq 6 the inductive effect of an atom is proportional to the difference in electronegativity between the substituent atom and the reaction center (the radical center in this case). It is reasonable to assume that the electronegativity increases in the order anion < radical < cation, and thereby the inductive character of a given substituent atom will change from electron withdrawing to electron donating. Only in extreme cases, the effect of a given substituent atom will be electron withdrawing also for cations.

The terms C in Table 6 could then be seen as the average inductive electronegativities of positively charged and negatively charged atoms, respectively.

DEVIATIONS FROM THE GENERAL TRENDS

Deviations from the additive scheme have been explained in terms of possible resonance effects and saturation effects.[3] An alternative, and perhaps more plausible, rationale for the majority of the deviations is that the deviating points are derived from radicals where the redox behavior is not necessarily that of an X-centered radical. In the case of ionization potentials of C-centered radicals, the operational atomic parameters for N, O, and S deviate markedly from the trend described by eq 7 and the parameters in Table 6. The observed effects of these substituents are larger than what is expected from the atomic properties used in eq 7, and this could be accounted for if the redox center (i.e., the positive charge) is partly shifted to the heteroatom. This is quite plausible since all these heteroatoms contain lone-pair electrons. An analogous case has been observed for one-electron reduction potentials of aryl methyl chalcogenide radical cations in aqueous solution.[11]

For the alkyl-substituted O- and S-centered radicals we have rather large discrepancies between experimental ionization potentials and the corresponding values calculated from eq 7. One reason for this could simply be that the experimental uncertainties in these values are rather large (≈±1 eV) and some of the values are relatively old (ionization potentials have a tendency to change as the experimental techniques are improved).

A major problem when calculating electron affinities from eq 7 is that we are unable to predict negative values which, in turn, is mostly a consequence of the e^-_{calc} for carbon being much too positive. The reason for this can be found in the approach we have used (eq 8). Since hydrogen, by definition, should have an e^--value of 0, eqs 7 and 8 should be 0 when the parameters for hydrogen are inserted. The problem is that carbon has the same electronegativity as hydrogen and the e^--value for carbon can therefore never be lower than 0 if the coefficient A is positive and $C < 2.10$. Considering the uncertainties in A and B, C could very well be somewhat higher than 2.10 which would put the effects of hydrogen and carbon in the right order.

CONCLUSIONS

Substituent effects on ionization potentials and electron affinities of C-, N-, O-, and S-centered radicals can be described quantitatively in terms of electronegativity and covalent radius of the substituting atoms. The main substituent effects on both the ionization potentials and electron affinity can be attributed to the ionic species rather than the radical. The nature of these effects is mainly inductive.

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