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REVISED METHOD FOR CALCULATION OF GROUP ELECTRONEGATIVITIES

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Since Wilmshurst's method for calculation of group electronegativity has some defects, the revised method was proposed for counting the number of valence electrons (n^*) on the central atom A in radical –AB, and group electronegativities of more than 150 substituents were reasonably calculated.

Electronegativity (χ) introduced by Pauling[1)] is one of the very useful concept in whole field of chemistry. Although several methods have been proposed for evaluating electronegativity,[2,3)] Gordy's[4)] and related definitions[5)] as covalent boundary potential and forces have a merit of simplicity to calculate an electronegativity of an atom.

We previously proposed new inductive substituent parameter (ι)[6)] to remove a periodicity for χ and also reported a linear relationship between ι values and Gordy's electronegativities (χ_G) for atoms.[7)] Since Wilmshurst[8)] has modified Gordy's method to calculate group electronegativity (χ_W), we used χ_W values to calculate ι values for the second period groups.[6)] However, we found some defects in the reported method[8)] during the course determining ι values of every substituents in the periodic table.

The present paper proposes a revised method for calculation of group electronegativity of every radicals -AB as shown in Eq. (1) for counting the number of valence electrons (n^*) on the central atom A;

$$n^* = (N-p) + 2m \frac{\chi_B}{\chi_A + \chi_B} - s \frac{\chi_A}{\chi_A + \chi_B} \qquad (1)$$

where N is the number of valence electron on the free atom A, p is the number of valence electrons incorporated from B to form the AB bond, m is the number of bond between A and B, s is the number of resonance contribution of $^-AB^+$ type, and χ_A and χ_B represent χ_G of atoms A and B, respectively. Then group electronegativity is calculated by the Gordy's equation;[4)]

$$\chi = 0.31 \left(\frac{n^* + 1}{r_A}\right) + 0.50 \qquad (2)$$

where r_A is the covalent radius of the atom A in the radical -AB.

Wilmshurst[8)] used the form $2m\cdot\chi_A/(\chi_A + \chi_B)$ for the second term in Eq. (1), opposite sign for the third term, and a slightly different definition for p.

Therefore, Wilmshurst's method[8)] gave relatively larger value than Huheey's value (χ_H)[9)] based on orbital electronegativity and values derived from some experimental data for groups containing the second period central atoms (e.g.: χ_W 2.88, χ_H 2.66, others 2.63,[10a)] 2.62[10b)] for CCl_2; χ_W 3.89, χ_H 3.51, others 3.51,[10c)] 3.6[10d)] for OH), and always gave lower values than χ_G for the same central atoms for groups containing higher period central atoms bonded to more electronegative groups (Table 1). The tendency is not the case. Moreover, the use of the third term was arbitrary, but, in Eq. (1), the use of the third term was limited to the groups having the structure of $C{=}\dot{A}{-}\ddot{B}$.

Table 1. Comparison of χ_W[a)] with χ_G (atom)[4)]

Period	Group	χ_W	χ_G	Group	χ_W	χ_G	Group	χ_W	χ_G
III	$-\underline{\mathrm{Mg}}\mathrm{Br}$	1.08	1.16	$-\underline{\mathrm{Si}}\mathrm{Me}_3$	1.68	1.82	$-\underline{\mathrm{P}}\mathrm{Ph}_2$	2.09	2.19
IV	$-\underline{\mathrm{Zn}}\mathrm{Me}$	1.12	1.21	$-\underline{\mathrm{Ge}}\mathrm{Me}_3$	1.62	1.77	$-\underline{\mathrm{As}}\mathrm{Ph}_2$	1.93	2.04
V	$-\underline{\mathrm{Cd}}\mathrm{Me}$	1.05	1.13	$-\underline{\mathrm{Sn}}\mathrm{Me}_3$	1.45	1.61	$-\underline{\mathrm{Sb}}\mathrm{Ph}_2$	1.70	1.82
VI	$-\underline{\mathrm{Hg}}\mathrm{Me}$	1.04	1.12	$-\underline{\mathrm{Pb}}\mathrm{Me}_3$	1.40	1.56	$-\underline{\mathrm{Bi}}\mathrm{Ph}_2$	1.71	1.83

a) Calculated by the Wilmshurst's method.[8)]

As seen from Eq. (2), χ value becomes large as the n* value increases. On the other hand, the χ value of group –AB should be enhanced by electronic deshielding on the A atom. Thus deshielding or shielding term should be positive or negative sign, respectively. Therefore, we used a positive sign and χ_B in the numerator as the second term in Eq. (1) because of a deshielding effect by the B atom, and a negative sign and χ_A in numerator as the third term because of a shielding effect by the B atom in $C{=}\dot{A}{-}\ddot{B}$ group. According to the modified definition for p, the sign of which is also in agreement with the above consideration, calculation for charged groups became possible.

Wilmshurst[8)] has arbitrarily utilized two types of r_A values in Eq. (2), which were taken from microwave spectroscopic data or Pauling's covalent radii. In order to calculate r_A of atom A in radical –AB, we applied the Schomaker-Stevenson's equation[11)] to evaluate equilibrium length of polar bond, and covalent radius, r_A, was obtained using Eq. (3);

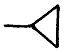
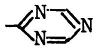
$$r_A = [r^\circ_A + r^\circ_B - 0.09|\chi_A - \chi_B|]r^\circ_A/(r^\circ_A + r^\circ_B) \qquad (3)$$

where r°_A and r°_B are Pauling's covalent radii for atoms A and B, respectively. The r_A values thus obtained were in a quite agreement with those derived from microwave spectroscopic data.

Thus, one can calculate group electronegativities of all substituents using Eqs. (1), (2), and (3). The calculated values of group electronegativities are summarized in Table 2. The χ_G values[7)] are used for Li, F, Cl, Br, and I atoms.

That the values thus obtained are reasonable was shown from the inspection of

Table 2. Group electronegativities

Group	χ	Group	χ	Group	χ	Group	χ
-H	2.176	-CF$_3$	2.985	-AlMe$_2$	1.658	-GeMe$_3$	1.943
-BeH	1.492	-CCl$_3$	2.666	-SiHMe$_2$	1.967	-GePh$_3$	1.996
-BH$_2$	1.981	-CBr$_3$	2.561	-SiMe$_3$	1.990	-GeF$_3$	2.235
-B(OH)$_2$	2.270	-CHO	2.866	-SiEt$_3$	1.993	-GeCl$_3$	2.044
-CH$_3$	2.472	-COMe	2.864	-SiPhMe$_2$	2.009	-AsMe$_2$	2.118
-Et	2.482	-COCF$_3$	2.938	-SiPh$_3$	2.047	-AsPh$_2$	2.161
-n-Pr	2.483	-COPh	2.681[a]	-SiF$_3$	2.299	-SeMe	2.373
-i-Pr	2.493	-COCN	2.972	-SiMeCl$_2$	2.061	-SeCF$_3$	2.419
-CHMeEt	2.494	-CONH$_2$	2.731[a]	-SiCl$_3$	2.099	-SePh	2.407
-t-Bu	2.501	-COOH	2.824[a]	-SiBr$_3$	2.028	-SeCN	2.475
	2.495	-COOR	2.832[a]	-PH$_2$	2.190	-CdMe	1.246
-CH=CH$_2$	2.785	-COCl	2.729[a]	-PMe$_2$	2.249	-InMe$_2$	1.533
-CH=CHMe	2.787	-CSNH$_2$	2.542[a]	-PPh$_2$	2.298	-SnMe$_3$	1.793
-CH=CHNO$_2$	2.807	-CN	3.208	-P(CN)$_2$	2.390	-SnEt$_3$	1.795
-Ph	2.717	-NH$_2$	2.992	-P(NMe$_2$)$_2$	2.354	-SbMe$_2$	1.924
-C≡CH	3.074	-NHMe	3.031	-PF$_2$	2.527	-SbPh$_2$	1.960
-C≡CPh	3.080	-NHAc	3.034	-PCl$_2$	2.343	-TeMe	2.130
-CH$_2$CF$_3$	2.537	-NHCOCF$_3$	3.033	-P(O)Me$_2$	2.472	-IO$_2$	2.833
-CH$_2$Ph	2.507	-NHCOPh	3.024	-P(O)Ph$_2$	2.519	-HgMe	1.237
-CH$_2$CONH$_2$	2.508	-NHCONH$_2$	3.031	-PO(OR)$_2$	2.419[a]	-HgCF$_3$	1.271
-CH$_2$COOH	2.520	-NHCSNH$_2$	3.033	-POCl$_2$	2.305[a]	-HgCN	1.285
-CH$_2$CN	2.563	-NHNH$_2$	3.033	-P(S)Ph$_2$	2.398	-HgOAc	1.304
-CH$_2$NH$_2$	2.538	-NMe$_2$	3.012	-P(S)Cl$_2$	2.135[a]	-HgCl	1.266
-CH$_2$NMe$_2$	2.542	-NEt$_2$	3.011	-SH	2.616	-PbMe$_3$	1.752
-CH$_2$NO$_2$	2.584	-N=C=O	3.552	-SMe	2.592	-PbEt$_3$	1.753
-CH$_2$OH	2.591	-N=C=S	3.505	-SEt	2.591	-BiPh$_2$	1.970
-CH$_2$OMe	2.597	-N=NPh	3.505	-SCF$_3$	2.652	-COO$^-$	2.779[a]
-CH$_2$OAc	2.592		2.927	-SPh	2.609	-O$^-$	3.194
-CH$_2$F	2.636	-NO	3.571	-SAc	2.631	-PO$_3$H$^-$	2.379
-CH$_2$SiMe$_3$	2.454	-NO$_2$	3.421[a]	-SF$_5$	3.076	-S$^-$	2.388
-CH$_2$SO$_2$CF$_3$	2.541	-OH	3.494	-SOMe	2.841	-SO$_3^-$	2.926[a]
-CH$_2$Cl	2.538	-OMe	3.543	-SOPh	2.859	-CH$_2\overset{+}{\mathrm{N}}H_3$	2.615
-CH$_2$Br	2.502	-OEt	3.544	-SO$_2$Me	2.998	-$\overset{+}{\mathrm{C}}$Me$_2$	3.168
-CH$_2$SnMe$_3$	2.435	-OCF$_3$	3.486	-SO$_2$CF$_3$	3.043	-$\overset{+}{\mathrm{N}}$H$_3$	3.711
-CH$_2$I	2.476	-OPh	3.525	-SO$_2$Ph	3.014	-$\overset{+}{\mathrm{N}}$Me$_3$	3.653
-CHPh$_2$	2.532	-OCHO	3.507	-SO$_2$NH$_2$	2.736[a]	-$\overset{+}{\mathrm{N}}$≡N	4.934
-CH(CN)$_2$	2.653	-OAc	3.510	-SO$_3$Et	2.816[a]	-$\overset{+}{\mathrm{O}}$Me$_2$	4.320
-CHF$_2$	2.807	-OSO$_2$Me	3.474	-SO$_2$Cl	2.734[a]	-$\overset{+}{\mathrm{P}}$Me$_3$	2.752
-CHCl$_2$	2.602	-OSO$_2$Ph	3.471	-ZnMe	1.336	-$\overset{+}{\mathrm{S}}$Me$_2$	3.095
-CHBr$_2$	2.532	-MgBr	1.295	-GaMe$_2$	1.658		

a) Corrected by resonance contribution (see text).

ι values for groups by three methods.[12)]

Correlation of J_{HH}^{trans} values in monosubstituted ethenes[13)] with χ_W or the present values (χ) for the second period groups also indicated adequacy of the present values as follows:

$$J_{HH}^{trans} = -3.6\,\chi_W + 27.4 \quad (r = 0.969,\ n = 11)$$

$$J_{HH}^{trans} = -3.8\,\chi + 27.7 \quad (r = 0.981,\ n = 11)$$

Very recently, Reynolds et al.[14)] have reported $(1-q_H)$ values calculated by ab initio method (6-31 G* level) for a series of H-X as a measure of substituent electronegativities. The correlation of $(1-q_H)$ with the present χ values is also much better than with χ_W as follows:

$$(1-q_H) = 0.266\,\chi_W - 0.565 \quad (r = 0.908,\ n = 13)$$

$$(1-q_H) = 0.298\,\chi - 0.631 \quad (r = 0.965,\ n = 13)$$

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