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ORIGIN OF AMPHIELECTRONIC EFFECT OF σ- AND π-ELECTRON-WITHDRAWING GROUPS ON σ^- APPLICATION SYSTEMS AND ELECTRON-DEFICIENT SYSTEMS

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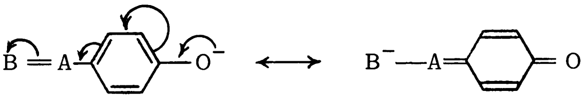
Nonlinearity of data for σ- and π-electron-withdrawing groups (EWG) with $\Delta\iota$ values in σ^- application systems was improved by consideration of difference of electronegativities between atoms A and B in substituent -A=B. This idea was also applied to π-donating effect of EWG in very electron-deficient system such as XCH_2^+.

We reported previously that the σ_I, σ, and σ° values of the σ- and π-electron-withdrawing groups (EWG) showed an excellently linear plot with the inductive substituent parameters, ι, (Gk: iota) values,$^{1)}$ and that the corresponding σ^- values, on the contrary, showed a very scattered plot against the ι or $\Delta\iota(= \iota_X - \iota_H)$ values. The linearity in the former cases indicates that the magnitude of resonance effect in EWG is generally proportional to the $\Delta\iota$ value. Thus the scattered plot for the σ^- values is attributed to the contribution of an extra resonance between a substituent and an electron-rich reaction center as known. This paper describes on the origin of the extra resonance.

We now consider a phenoxide anion possessing a B=A- group at the para position (1) as an example. It is expected that the contribution of the extra resonance in 1 would increase as the difference in the electronegativities (χ) of the atoms A and B in the substituent -A=B ($\Delta\chi = \chi_B - \chi_A$) becomes larger, because the polarization in the -A=B bond increases and the positive charge on the atom A becomes larger. Thus, Eq. 1 is expected to be applicable to the σ^- application systems. In Eq. 1 , δ and c denote a relative data and a deviation in the data of parent compound, respectively, a and b'(= ab) represent a sensitivity for $\Delta\iota$



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$$\delta = a\cdot\Delta\iota + b'\cdot\Delta\chi + c = a(\Delta\iota + b\cdot\Delta\chi) + c \qquad (1)$$

and $\Delta\chi$ values, respectively, the Gordy's atom electronegativity $(\chi_G)^{2)}$ is used because the χ_G value was used in the calculation of the ι value,$^{1,3)}$ and the $\Delta\iota$ value is independent of the $\Delta\chi$ value.

Table 1. Application of Selected Data to Eq. 1

No	System	a	b	c	n[a)]	r[b)]	Ref.
1	$\delta\Delta G(g)(MeX)$	57.24	0.460	-0.44	7	0.995	4,5
2	$\delta\Delta E(4\text{-}31G)(XCH_2^-)^{c)}$	-104.6	0.212	1.5	4	0.968	5,10
3	$\delta\Delta E(STO\text{-}3G)(XCH_2^-)^{c)}$	-119.6	0.239	0.2	4	0.9999_6	5,10
4	$\Delta pKa(aq)(CH_2XY)$	-18.62	0.492	0.34	10	0.977	11
5	σ_p^-	1.40	0.265	-0.03	7	0.983	15
6	$\delta\Delta G(g)(p\text{-}XC_6H_4OH)$	-25.10	0.164	-0.03	7	0.985	6
7	$\delta\Delta G(aq)(p\text{-}XC_6H_4OH)$	-4.25	0.276	0.08	7	0.955	6
8	$\delta\Delta E(STO\text{-}3G)(p\text{-}XC_6H_4OH)$	35.91	0.089	-1.88	5	0.978	12
9	$\delta\Delta G(g)(p\text{-}XC_6H_4N\underline{H}_2)$	-25.67	0.173	0.17	6	0.992	7
10	$\Delta pKa(aq)(p\text{-}XC_6H_4NH_2)$	-4.18	0.177	-0.03	5	0.999	14
11	$\delta\Delta E(STO\text{-}3G)(p\text{-}XC_6H_4N\underline{H}_2)$	33.76	0.101	-1.82	5	0.978	12b,13
12	$\delta\Delta G(g)(p\text{-}XC_6H_4C\underline{H}_3)$	-26.71	0.261	0.57	6	0.979	8
13	$\delta\Delta E(STO\text{-}3G)(p\text{-}XC_6H_4C\underline{H}_3)$	38.65	0.105	-2.13	5	0.976	12b
14	σ_I	0.891	-0.028	0.016	9	0.985	16
15	σ_m^o	0.975	-0.020	0.011	7	0.995	16
16	σ_p^o	1.078	0.044	0.007	7	0.997	16
17	σ_m	0.993	0.018	-0.008	9	0.997	16
18	σ_p	1.023	0.046	0.027	9	0.992	16
19	$\delta\Delta G(g)(p\text{-}XC_6H_4CO_2H)$	-16.28	0.013	-0.06	6	0.986	8
20	$\delta\Delta G(g)(m\text{-}XC_6H_4OH)$	-20.9	-0.062	-0.02	7	0.979	6
21	$\delta\Delta G(aq)(m\text{-}XC_6H_4OH)$	-3.03	-0.010	0.01	6	0.999	6
22	$\Delta pKa(aq)(m\text{-}XC_6H_4NH_2)$	-2.88	0.021	0.08	6	0.989	14
23	$\delta\Delta E(STO\text{-}3G)(p\text{-}XC_6H_5\cdots\ominus)$	-18.03	-0.055	0.91	5	0.971	17
24	$\delta\Delta E(4\text{-}31G)(XCH_2^+)^{c)}$	73.7	-0.322	-0.9	4	0.929	5,10

a) Number of substituents examined. b) Correlation coefficient. c) These values were calculated by the combination of the results by us[10)] with those by Reynolds et al.,[5)] where the energies for XCH_2^+ and XCH_2^- were calculated using the standard values as planar charged center.

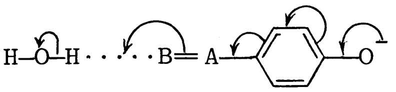
As the σ_p^- application systems, changes in the gas phase acidities ($\delta\Delta G(g)$; kcal/mol) of CH_3X,[4,5)] $p\text{-}XC_6H_4OH$,[6)] $p\text{-}XC_6H_4N\underline{H}_2$,[7)] and $p\text{-}XC_6H_4C\underline{H}_3$,[8)] the relative energy changes ($\delta\Delta E$; kcal/mol) for the isodesmic reactions[9)] of XCH_2^- (at STO-3G and 4-31G levels),[5,10)] $p\text{-}XC_6H_4O^-$ (at STO-3G level),[12)] $p\text{-}XC_6H_4NH^-$ (at STO-3G level),[12b,13)] and $p\text{-}XC_6H_4CH_2^-$ (at STO-3G level),[12b)] changes in the liquid phase acidities ($\delta\Delta G(aq)$; kcal/mol) of $p\text{-}XC_6H_4OH$,[6)] the relative pKa values ($\Delta pKa(aq)$) of CH_2XY[11)] and $p\text{-}XC_6H_4NH_2$,[14)] and the σ_p^- values[15)] were selected. The results of their application to Eq. 1 are shown in Nos. 1-13 of Table 1, indicating a good fitness of Eq. 1 . On the other hand, in the nonextra resonance systems such as the σ_I, σ_m^o, σ_p^o, σ_m, and σ_p values,[16)] $\delta\Delta G(g)$ of $p\text{-}XC_6H_4CO_2H$[8)] and $m\text{-}XC_6H_4OH$,[6)] $\delta\Delta G(aq)$ of $m\text{-}XC_6H_4OH$,[6)] $\Delta pKa(aq)$ of $m\text{-}XC_6H_4NH_2$,[14)] and $\delta\Delta E$ (at STO-3G level) of the $p\text{-}XC_6H_5\cdot\cdot\ominus$ systems,[17)] the b value in Eq. 1 was nearly zero in each case as expected (Nos. 14 - 23 of Table 1).

These results confirm the validity of Eq. 1. Thus, the origin of the substituent effect in the $\bar{\sigma}_p$ application systems was elucidated to result from an extra through-bond resonance effect between an electron-rich center and polarized -A=B bond.

The Taft's β scale (hydrogen-bond acceptance)[18] of the solvent such as C_6H_5-EWG or the effect of hydration to the EWG group shows a similar trend to the π-acceptance in XCH_2^-.[5] Actually Eq. 1 was applicable as shown in Eq. 2.

$$\beta = 0.27(\Delta\iota + 0.910\cdot\Delta\chi) + 0.11 \qquad (n=7,\quad r=0.969) \qquad (2)$$

In the cases of p-XC_6H_4OH, the b values in aqueous solution (Nos. 5 and 7) are larger than that in gas phase (No. 6), because of a contribution of the effect shown in Eq. 2. This fact may be attributed to the increase of the positive charge density on the atom A by hydration as shown in 2. Therefore, it is concluded that the b value may reflect the extent of an extra resonance between substituent and reaction center.



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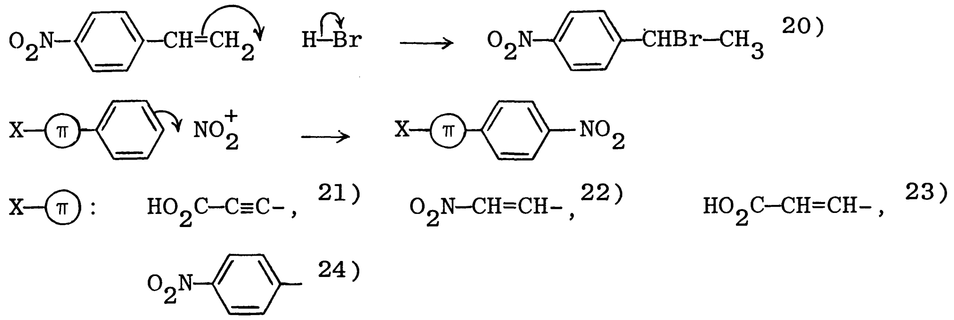
Secondly, a π-electron-donating effect (amphielectronic nature[5]) of EWG toward a very electron-deficient center such as that in XCH_2^+ ion has recently received much attention.[5,19] In a carbocation B=A-CH_2^+ it is expected that the π-donation would increase as the Δχ value in -A=B becomes smaller, and thus that Eq. 1 would be also applied even to this case to give a negative b value. As shown in No. 24 of Table 1, in fact, the expectation was true. In these systems, the inductive destabilization and the conjugative stabilization are operative competitively.

Thus it was established that Eq. 1 can estimate the amphielectronic extra resonance effect of EWG in all systems from the extent of the polarization in the B=A- bond.

This idea is useful for the prediction of regioselectivity in the electrophilic additions and substitutions. For example, the regioselectivity in the following cases is explicable by a fact that a very small Δχ value in the carbon-carbon π-bond concerned makes the π-donation easy.



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