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SUBSTITUENT ELECTRONEGATIVITY PARAMETER AS THE ORIGIN OF FIELD EFFECT IN ALIPHATIC SYSTEMS

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Summary: Linear relationship between substituent electronegativity parameter ($\Delta\iota$ or σ_χ) and field parameter ($\sigma_I(g)$) was obtained by using the charge separation parameter (λ) between positive and negative poles in H-X molecule calculated by ab initio MO method.

An elucidation of a role of group electronegativity in the field effect may cast a light on the interpretation of electronic effect of substituent in the multiparameter Hammett equation.[1] Previously we pointed out that the inductive substituent parameters (ι) based on electronegativity were not linearly related to the field parameters (σ_I).[2] Recently, Reynolds[3] and Taft et al.[4] have also indicated the nonlinearity in the plot of the observed dipole moments of substituted methanes (p_{MeX}) against the group electronegativities[3] and also in the plot of the substituent electronegativity parameters (σ_χ), which were determined from the charge ($1 - q_H$) on the hydrogen in H-X calculated at 6-31G* level,[4] against the substituent field parameters (σ_F).[4b]

We wish to report here that a linear relationship between the inductive substituent ($\Delta\iota$ ($= \iota_X - \iota_H$))[6c] or the substituent electronegativity parameter (σ_χ)[4] and the field parameter ($\sigma_I(g)$)[5] defined from phenol acidities in gas phase was obtained by using the following equations,

$$\sigma_I(g) = 0.470 \cdot \Delta\iota \cdot \lambda \qquad (r = 0.985, \quad n = 11) \qquad (1)$$

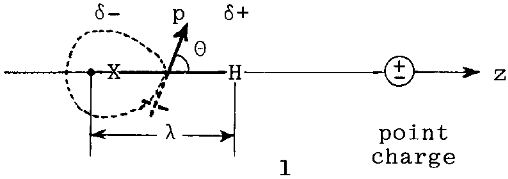
$$\sigma_I(g) = 0.972 \cdot \sigma_\chi \cdot \lambda \qquad (r = 0.984, \quad n = 11) \qquad (2)$$

where λ is the distance between positive and negative poles in H-X molecule as represented schematically in 1. The $\Delta\iota \cdot \lambda$ and $\sigma_\chi \cdot \lambda$ terms are proportional to the z-component of the dipole moment of H-X molecule (i.e., $p_z = p \cdot \cos\theta$; see 1). Moreover, it has been shown that the $\Delta\iota$ value, which is proportional to $\Delta\chi$ of the substituents in the same period,[6c] is proportional to the charge ($1 - q_H$) on

Table 1. The charges on hydrogen ($1 - q_H$), z-components of dipole moments (p_z), and the distances of charge separation (λ) in H-X molecules.

Substituent	4-31G[a]			6-31G[a]		
	$1 - q_H$	p_z (D)[b]	λ (Å)	$1 - q_H$	p_z (D)[b]	λ (Å)
CH_3	0.1522	0.00	0.000	0.1549	0.00	0.000
NH_2	0.3042	0.73	0.500	0.3086	0.73	0.495
OCH_3	0.3967	1.24	0.651	0.3977	1.24	0.649
OH	0.3936	1.60	0.846	0.4257	1.62	0.796
CHO	0.1541	1.57	2.121	0.1484	1.58	2.221
F	0.4786	2.28	0.992	0.4820	2.30	0.992
CF_3	0.2104	2.17	2.147	0.1972	2.20	2.320
$COCH_3$	0.1559	1.20	1.603	0.1498	1.21	1.682
CN	0.3308	3.25	2.046	0.3336	3.27	2.039
NO_2	0.4320	3.51	1.692	0.4247	3.53	1.733

a) The molecular geometries were taken from experimentally determined values, (cf. ref. 6a). b) $p_z = p\cdot\cos\Theta$ in Debye unit.



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the hydrogen atom in the H-X molecule.[6b]

The values of ($1 - q_H$), p_z, and λ calculated at 4-31G and 6-31G levels are given in Table 1. The $\Delta\iota\cdot\lambda$ and $\sigma_\chi\cdot\lambda$ values were plotted against $\sigma_I(g)$ in Fig. 1, where the average values at 4-31G and 6-31G levels were used as λ ($\lambda = p\cdot\cos\Theta/[e(1 - q_H)]$). These results confirmed that the product of the substituent electronegativity parameter, $\Delta\iota$ or σ_χ, and the charge separation parameter (λ), that is, the z-component dipole moment (p_z) is the origin of the field effect in HX molecule. In fact, the following equations were obtained:

$\sigma_I(g) = 0.192\cdot p_z$ at 4-31G level ($r = 0.988$, $n = 11$)

$\sigma_I(g) = 0.190\cdot p_z$ at 6-31G level ($r = 0.988$, $n = 11$)

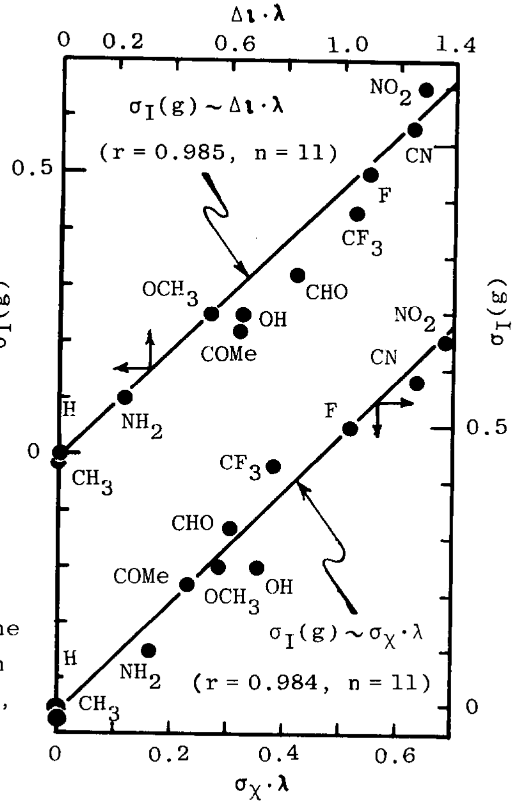


Fig. 1. Relationship between field parameter $\sigma_I(g)$ and $\Delta\iota\cdot\lambda$ or $\sigma_\chi\cdot\lambda$ term.

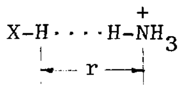
Table 2. Statistical analysis of substituent effects on acid dissociation constants ($\log(K/K_H)$) of 2 - 4.

System	Parameter	Slope	r[a)]	SD[b)]	f[c)]	n
2	$\Delta\iota\cdot\lambda$	2.07	0.966	0.26	0.18	9
	$\sigma_X\cdot\lambda$	3.93	0.957	0.33	0.19	9
3	$\Delta\iota\cdot\lambda$	0.75	0.973	0.16	0.16	7
	$\sigma_X\cdot\lambda$	1.43	0.973	0.11	0.17	7
4	$\Delta\iota\cdot\lambda$	2.34	0.990	0.22	0.12	7
	$\sigma_X\cdot\lambda$	4.59	0.991	0.23	0.12	7

a) Correlation coefficient. b) Standard deviation. c) Goodness of fit (SD/RMS). RMS denotes the root mean square of the data.

In connection with recent report,[3] the acid dissociation constants of substituted acetic acids (2), 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (3), and 4-substituted quinuclidinium ion (4) were selected.[3] The results of the statistical analysis of the relative dissociation constants using the new term, $\Delta\iota\cdot\lambda$ or $\sigma_X\cdot\lambda$, in HX are given in Table 2. They show a good correlation in each system. Therefore, the origin of the field effect[6a] of substituent is attributed to the z-component of the dipole (i.e., $p\cdot\cos\Theta$) caused by the group electronegativity of substituent.

Marriott and Topsom[7] have recently calculated a theoretical scale of field parameter ($\sigma_{F(theor)}$) for a wide variety of substituents by using a hypothetical proton transfer process in an isolated molecule system at a longer distance (r = 4.5 Å or above). In order to explore the origin of the field interaction energy caused by substituent dipole close to probe center, we



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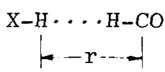
(X = H, NH_2, F, NO_2)



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$$(\mathrm{X{-}H\cdots NH_3}) + (\mathrm{H{-}H\cdots H\overset{+}{N}H_3}) \longrightarrow (\mathrm{H{-}H\cdots NH_3}) + (\mathrm{X{-}H\cdots H\overset{+}{N}H_3}) \qquad (3)$$

$$(\mathrm{X{-}H\cdots HCO_2H}) + (\mathrm{H{-}H\cdots HCO_2^-}) \longrightarrow (\mathrm{H{-}H\cdots HCO_2H}) + (\mathrm{X{-}H\cdots HCO_2^-}) \qquad (4)$$

Table 3. Relative isodesmic reaction energies ($\delta\Delta E$) and its component energies[a)] for Eqs.(3) and (4) at 4-31G level (in kcal mol^{-1}).[b)]

System		r (Å)	δΔE	δES	δPL	δCT	δEX	δMIX
$H_3\overset{+}{N}H\cdots\cdot$	H-NH_2	2.5	7.64	8.93	-4.69	-3.76	4.53	2.63
	H-F		20.98	23.74	-2.95	-3.70	2.43	1.46
	H-NO_2		27.10	30.55	-5.47	-3.62	3.51	2.13
$^-O_2CH\cdots$	H-NH_2	2.5	2.89	-6.44	-2.00	-4.27	14.19	1.41
	H-F		-7.52	-11.02	-4.21	-4.13	10.05	1.79
	H-NO_2		-12.90	-16.50	-6.45	-5.27	12.59	2.73

a) Negative sign denotes stabilization energy. b) 1 cal = 4.184 J.

carried out the energy decomposition analysis[8] for the relative energies ($\delta\Delta E$) of the proton transfer isodesmic reactions [Eqs. (3) and (4)] for molecular pairs 5 and 6 at various distances (r = 4.5, 3.5, 2.5, 2.25, and 2.0 Å) by ab initio MO method at 4-31G level. The distance r was taken from the H atom in H-X to the charged N atom or the carbonyl carbon atom. The relative interaction energy ($\delta\Delta E$) was divided into the five components as follows:

$$\delta\Delta E = \delta ES + \delta PL + \delta CT + \delta EX + \delta MIX$$

where the relative component energy δES means electrostatic, δPL polarization, δCT charge transfer, δEX electron exchange repulsion, and δMIX the higher order terms. Typical data of the energies ($\delta\Delta E$) and its energy components for the molecular pairs 5 and 6 are shown in Table 3 only for the case of r = 2.5 Å. The δES term is generally predominant in $\delta\Delta E$, except for 6 at distances shorter than 3 Å where the δEX term considerably contributes to $\delta\Delta E$. Figure 2 shows that the δES term in 5 and 6 correlate with the parameter, $\Delta\iota\cdot\lambda$, even in shorter distances.

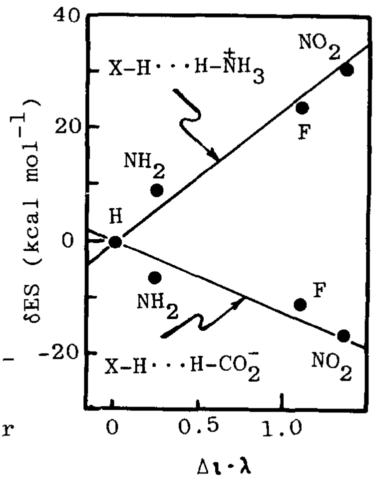

Fig. 2. Relationship between δES and $\Delta\iota\cdot\lambda$ in 5 and 6 at r=2.5 Å.

Thus, it was shown that $\Delta\iota$ or σ_X is correlated with the field parameter, $\sigma_I(g)$ and σ_F, by using the charge separation parameter (λ).

This study is being extended to other substituents and systems.

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