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TAFT'S SUBSTITUENT CONSTANTS, σ^* AND σ_I, AND HUHEEY'S GROUP ELECTRONEGATIVITY

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For 34 groups, Taft's substituent constants σ^* and σ_I are found to correlate well ($r = 0{\cdot}962$ and $0{\cdot}948$) with Huheey's group electronegativity (χ^H) when Taft's steric parameter E_s for a group is mixed with σ^* and σ_I:

$$\chi^H = 0{\cdot}360(\sigma^* - 0{\cdot}107\ E_s) + 2{\cdot}255$$

$$\chi^H = 3{\cdot}048(\sigma_I - 0{\cdot}014\ E_s) + 2{\cdot}196$$

From these equations, it follows that for a particular chemical group G, $\sigma^*(G) \approx 8\sigma_I(G)$. Since the σ^* scale is essentially based on the σ_I scale, the small inherent steric component in σ_I is amplified in the case of the σ^* by a factor of *ca* 8. An analysis shows that χ^H represents the electronegativity of a group when the group is considered to be a mere collection of non-bonded, charged and suitably hybridized atoms. Thus σ^* and σ_I are found to represent the electronegativity of a group in the spirit of the χ^H. It is concluded that a chemical group can be viewed as a collection of non-interacting atoms. Although there is evidence that a molecule can sometimes be treated similarly, for a group such a situation is novel.

INTRODUCTION

The term σ_I is the inductive component of Hammett's σ, an empirical parameter derived thermodynamically in the 1930s and applicable to aromatic substituents.[1–3] Its alkyl counterpart, σ^* was derived kinetically by Taft in the 1950s.[4] The relationship between these two parameters is given by the following equation according to Taft,[3] where G is a chemical group:

$$\sigma_I(G) = 0{\cdot}45\sigma^*(CH_2G) \qquad (1)$$

However, opinions differ as to the real nature of σ^* and σ_I. A classically accepted notion is that these two parameters represent the electron-donating or -withdrawing power of G. The same notion is held for the electronegativity of a group (χ_G). Hence a very good test of the classical hypothesis would be to seek a correlation between χ_G and σ^* or σ_I. However, for many years the test(s) could not be performed reliably. The situation was summarized by Exner[5] recently: 'The main problem is extending the various definitions of electronegativities to groups. This was done arbitrarily and the results of the various methods may disagree considerably. Until recently, authentic group electronegativity scales were not available. Probably the best scale for group electronegativity (χ^P, where P represents Pauling) was derived in 1990 by applying Pauling's bond energy equation to polyatomic molecules of type HG with minor modifications.[6] It is significant that χ^P does not give rise to any appreciable correlation with σ^* and σ_I. Another very good theoretical group electronegativity scale proposed by Myllay[7](χ^M) also does not bear any relationship with σ^* or σ_I. The two available experimental scales for χ_G are based on ^{13}C NMR studies: $^1J_{CC}$ (*ortho–ipso*) coupling constants in monosubstituted benzenes[8,9] and Inamoto's *i* scale.[10,11] Neither of them can be correlated with σ^* and σ_I. Taft has shown[12] by high-level *ab inito* calculations on molecules of type HG that the group charge q_G does not bear any relationship with σ_I. Using Taft's q_G, we formulated[13] a group electronegativity scale χ^D which also does not correlate with σ_I. Although the list of such direct/indirect non-correlations of σ^*/σ_I with the concept of electronegativity is long, some meaningful correlations for σ_I and σ^* in this direction have been obtained in the past.

Topsom[14] found that the σ_I of a group G correlates well with the charge induced on an H atom of an H_2 molecule by a molecule HG kept at a distance of 4 Å:

$$\text{H—H} \qquad \longleftarrow 4\text{Å} \longrightarrow \qquad \text{H—G}$$

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They took this as a clear demonstration of the field nature (i.e. operation through space) of σ_I. We feel that this does not thwart the classical idea completely, since the charge on the H atom in HG, which is mainly responsible for the distant induction, is certainly governed by the electronic nature of G. This view is supported by the very good correlation of σ_I obtained by Charton[15] for groups of type —XY_n, where Y is a constant substituent (H or CH_3) in the equation

$$\sigma_I = a_1\chi_X + a_2n_Y + a_0 \qquad (2)$$

where χ_X is the electronegativity of X in the Allred–Rochow scale and n_Y is the number of Y groups bonded to X. The correlation is particularly meaningful in our context since for such groups [—XH_n or —$X(CH_3)_n$] the quantity $(\chi_X + a_2n_Y/a_1)$ is likely to describe some kind of group electronegativity of —XY_n.

A successful correlation for σ^* was obtained by Huheey.[16] He found that the charge on the ester group in $RCOOC_2H_5$ correlates linearly ($r = 0{\cdot}970$) with σ^* of the alkyl group R for 47 groups. However, in this group charge calculation he assumed 80 per cent equalization of electronegativity, which is not acceptable, on two counts: first, the percentage is *ad hoc*, and second, the complete equalisation of electronegativities of atoms on molecule formation is now well established.[17–19] Earlier Huheey[20] also developed a scale χ^H for group electronegativity which maintained the principle of equalization of electronegativity. Curiously he found[16] that such group electronegativities (for 50 groups) do not correlate well ($r = 0{\cdot}840$) with σ^*.

We have reanalysed the work of Huheey[16] in an attempt to understand the nature of σ^* and σ_I.

Table 1. Values of χ^H, σ^*, E_s and σ_I for the various groups used in this study[a]

No.	Group	$\chi^{H\,b}$	$\sigma^{*\,c}$	$-E_s{}^c$	$\sigma_I{}^d$
1	F_3C	3·46	2·55	2·40	0·40
2	Cl_3C	3·30	2·65	3·30	0·36
3	F_2CH	3·00	2·05	1·91	0·32
4	$CH_3OC(O)$	2·94	2·00		
5	Cl_2CH	2·99	1·94	2·78	
6	$CH_3C(O)$	2·69	1·65		
7	$C_6H_5C{\equiv}C$	2·61	1·35		
8	$H_3CS(O)_2CH_2$	2·85	1·32		
9	$NCCH_2$	2·96	1·30	2·38	0·20
10	FCH_2	2·61	1·10	1·48	
11	$HOC(O)CH_2$	2·99	1·05		
12	$ClCH_2$	2·64	1·05	1·48	0·17
13	$BrCH_2$	2·64	1·00	1·51	0·20
14	ICH_2	2·59	0·85	1·61	0·17
15	F_3CCH_2	2·89	0·92		
16	$C_6H_5OCH_2$	2·57	0·85	1·57	0·12
17	$C_6H_5C(OH)H$	2·60	0·76		
18	$CH_3C(O)CH_2$	2·53	0·60	1·99	
19	C_6H_5	2·49	0·60	3·79	0·12
20	$HOCH_2$	2·74	0·55	1·21	0·11
21	H_3COCH_2	2·53	0·52	1·43	0·11
22	H	2·21	0·49	0·00	0·00
23	$C_6H_5CH{=}CH$	2·48	0·41		
24	$(C_6H_5)_2CH$	2·48	0·405	2·67	
25	$ClCH_2CH_2$	2·49	0·385	2·14	0·07
26	$H_3CCH{=}CH$	2·37	0·36		
27	$F_3CCH_2CH_2$	2·70	0·32		
28	$C_6H_5CH_2$	2·45	0·215	1·62	0·03
29	$H_3CCH{=}CHCH_2$	2·45	0·13		
30	$F_3CCH_2CH_2CH_2$	2·60	0·12		
31	$C_6H_5C(CH_3)H$	2·42	0·11	2·43	0·07
32	$C_6H_5CH_2CH_2$	2·42	0·08	1·62	
33	$C_6H_5CH_2CH_2CH_2$	2·40	0·02	1·75	0·01
34	$C_6H_5C(C_2H_5)H$	2·40	0·04		
35	H_3C	2·27	0·00	1·24	−0·01
36	c-$C_6H_{11}CH_2$	2·29	−0·06	2·22	−0·03
37	C_2H_5	2·28	−0·10	1·31	−0·01
38	n-C_3H_7	2·28	−0·115	1·60	−0·01
39	i-C_4H_9	2·29	−0·125	2·17	−0·01
40	n-C_4H_9	2·29	−0·13	1·63	−0·01
41	c-C_6H_{11}	2·29	−0·15	2·03	0·00
42	$(CH_3)_3CCH_2$	2·29	−0·165	2·98	0·00
43	i-C_3H_7	2·28	−0·19	1·71	0·01
44	c-C_5H_9	2·29	−0·20		
45	s-C_4H_9	2·29	−0·21	2·37	−0·01
46	$(C_2H_5)_2CH$	2·29	−0·225	3·22	
47	$(CH_3)_3SiCH_2$	2·33	−0·26		
48	$(CH_3)_3C(CH_3)CH$	2·29	−0·28	4·57	
49	t-C_4H_9	2·29	−0·30	2·78	−0·01
50	O_2N	4·83		2·52	0·67
51	F	4·00		0·46	0·54
52	NC	3·84		0·51	0·57
53	H_3CO	2·68		0·55	0·30
54	HO	3·51		0·55	0·24
55	H_2N	2·61		0·61	0·17
56	$(CH_3)_3Si$	2·27		3·36	−0·11

[a] For the meanings of the symbols, see text.
[b] Values given in Pauling's unit taken from Refs 16 and 20.
[c] Data taken from Ref. 4.
[d] Data taken from Ref. 28.

RESULTS AND DISCUSSIONS

We have found that χ^H values correlate to some extent ($r = 0{\cdot}916$) with the σ^* values of 49 groups listed in Table 1. The list differs from that used by Huheey[16] only in the introduction of a new group CF_3 to extend the range of χ^H covered, and exclusion of two deviants, $CH_2N^+(CH_3)_3$ and $CH_2CH_2NO_2$. In a paper in which we used σ^* to understand the nature of the oxidative addition reactions,[21] we indicated that σ^* probably represents the inductive effect exerted by an alkyl group with some component of steric effect. This was, not new, however – many workers earlier[22] also drew the same conclusion. To test the validity of such a concept, we sought a correlation of Huheey's group electronegativity with σ^* and the steric parameter associated with a particular group. Although we have shown recently[23] that Dubois' steric parameter E_s' is better than Tafts E_s scale, here we chose to use Taft's scale[4] since the evaluations of σ^* and of E_s are intimately related. For 34 groups for which Taft's E_s values are available (Table 1), we found that the correlation coefficient r increases on mixing E_s with σ^* (the statistical technique adopted has been elaborated elsewhere[24]).

Mixing of 10·7 per cent of E_s with σ^* yields the best correlation [equation (3); $r = 0{\cdot}962$; Figure 1]:

$$\chi^H = 0{\cdot}360(\sigma^* - 0{\cdot}107\ E_s) + 2{\cdot}255 \qquad (3)$$

Since the steric factor appears with a negative sign in equation (3), it follows that in its absence a group would have been more electron donating. This observation is in line with general expectations. In the case of σ_I for 34 groups (Table 1), the best correlation ($r = 0{\cdot}948$) is obtained when only 1·4 per cent of E_s is mixed with σ_I [equation (4), Figure 2]

$$\chi^H = 3{\cdot}048(\sigma_I - 0{\cdot}014\ E_s) + 2{\cdot}196 \qquad (4)$$

As found for σ^*, for σ_I also the steric factor appears with a negative sign in equation (4). Although the percentage mixing of the steric factor is less in case of the σ_I parameters, the total steric mixing required is almost the same in both cases, as revealed by the equations

$$\chi^H = 0{\cdot}360\sigma^* - 0{\cdot}038E_s + 2{\cdot}255 \qquad (5)$$

$$\chi^H = 3{\cdot}048\sigma_I - 0{\cdot}043E_s + 2{\cdot}196 \qquad (6)$$

From these equations, it follows that for a particular group G, $\sigma^*(G) \approx 8\sigma_I(G)$. Hence the electronic factor is considerably attenuated in the σ_I parameters. This is probably because σ_I measures the electronic effect of a substituent present at the *meta* and *para* positions in benzoic acid, which is located further from the reaction centre than in the case of the σ-substituent of acetic acid. Our correlations show that σ_I inherently has a very small amount of steric component. This small amount of steric mixing is amplified in σ^*, with the amplification factor being *ca* 8. This is a direct consequence of the fact[22] that Taft's σ^* is essentially based on the σ_I scale. We conclude that σ^* or σ_I does represent, to a satisfactory extent, some kind of electronegativity of a group with a steric component.

The question now is why σ^* or σ_I does not correlate with χ^P, χ^M or χ^D or the experimental electronegativity scales. The answer is that Huheey's scale represents a different kind of group electronegativity from the other scales mentioned. To understand this, we must examine the nature of χ^H.

The variation of the electronegativity of an atom with the charge q on it is approximately given by the equation

$$\chi = \chi_0 + 2\eta q \qquad (7)$$

where χ_0 is the electronegativity and η the hardness of

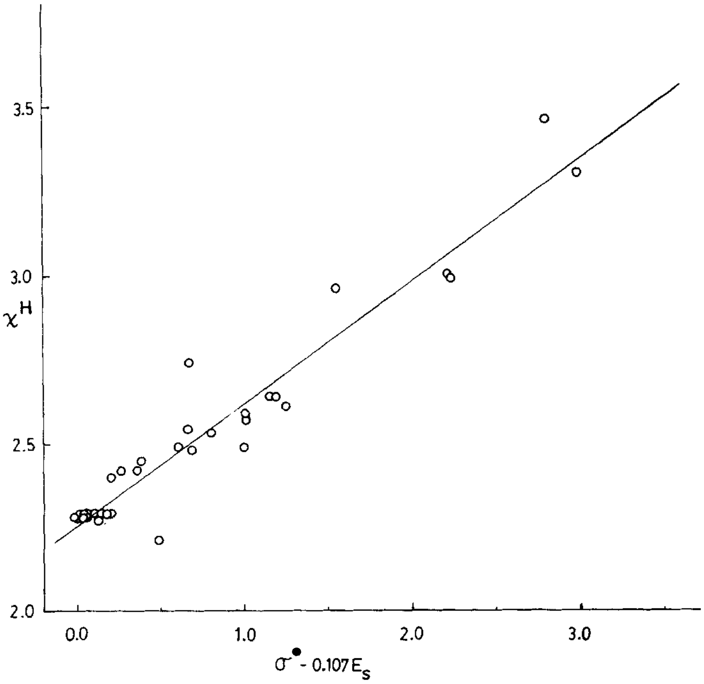

Figure 1. Variation of χ^H (Huheey's group electronegativity) with Taft's polar substituent parameter σ^* and steric parameter E_s; correlation coefficient $r = 0{\cdot}962$

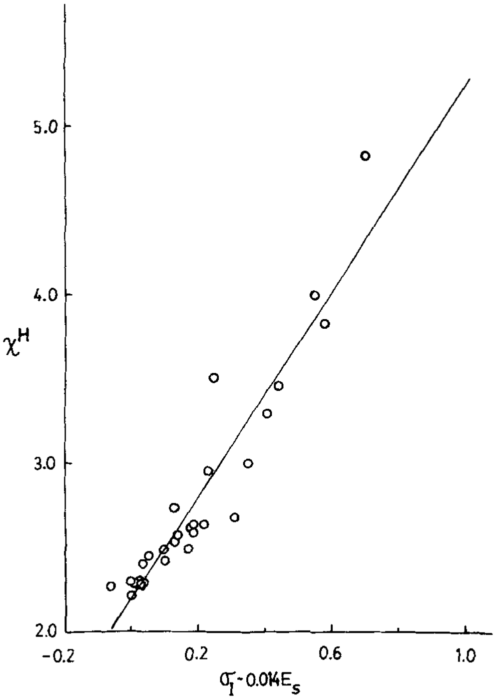

Figure 2. Variation of χ^H (Huheey's group electronegativity) with Hammett σ_I and Taft's steric parameter E_s; correlation coefficient $r = 0{\cdot}948$

the neutral ($q = 0$) atom.[25-27] Equation (7) was used by Huheey to evaluate the electronegativity of a group. In Huheey's method,[20] it can be shown that χ_0 of a group G (χ^H) is given by the equation

$$\chi^H = \left[\sum_i (\chi_{0,i}/2\eta_i)\right] \Big/ \left[\sum_i (1/2\eta_i)\right] \qquad (8)$$

where i refers to the ith atom member of the group G. It should be noted that even if all the atoms of the group G are 100 Å apart from each other, the same equation would be used. The point is that the features of bonding between the constituent atoms of a group have not been included explicitly to calculate the group electronegativity. Thus we realise that Huheey envisages a group as a mere collection of atoms which have some charges and are suitably hybridized to yield the proper geometry of the group (Huheey included the effect of hybridization of an atom on its χ_0 and η). Since the final features of the interatomic bonding in a group have been neglected, in Huheey's method electronegativities of the isomeric groups cannot be distinguished. This is not the case with χ^P, χ^M or χ^D, where the bonding features are included explicitly.

CONCLUSION

It is interesting that the correlation of χ^H with σ^* or σ_I *indicates that groups can be viewed as a mere collection* of atoms without any bonds between them. For groups such a revelation is really novel. However, there is experimental proof for the fact that a molecule can sometimes be treated as a collection of non-bonded atoms, viz. Sanderson's geometric mean principle of electronegativity equalization[17-19] and Datta's geometric mean principle for hardness equalization.[27]

The discussion would be incomplete if we did not mention that there has been controversy regarding the real nature of σ_I, although Taft originally defined it as an 'inductive electrical effect' parameter. The controversy actually revolves around the manner in which the 'inductive electrical effect' of a chemical group is transmitted: through space,[14] or through bonds, or through both.[28] However in the literature the σ^* parameters have always been referred to as polar parameters. Here we have shown that σ^* and σ_I are essentially of the same nature and mostly related to the same type of group electronegativity. Hence our correlation has an important bearing on the mode by which the parameters σ^* and σ_I transmit their effect onto the probing site.

The conclusions of this work are as follows. (i) Huheey's group electronegativity scale describes a group as a mere collection of non-bonded, charged and properly hybridized atoms. (ii) σ^* and σ_I actually represent the electronegativity of a group in the spirit of χ^H with a small component of steric effect. (iii) Compared with σ_I, the σ^* parameters suffer more from mixing of the steric parameter. Although the first two conclusions are new, the third has been reached earlier by several workers.[22]

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