Tetrahedron Letters,Vol.27,No.39,pp 4683-4686,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A COMPARISON OF GROUP ELECTRONEGATIVITY AND FIELD EFFECTS

E. Sacher
Groupe des Couches Minces
and
Département de Génie Physique
Ecole Polytechnique de Montréal
CP 6079, Succursale "A"
Montréal, Québec H3C 3A7
Canada

SUMMARY: A statistical analysis used to demonstrate that the two group electronegativity scales, one thought to represent through-bond effects and the other, through-space effects, in fact differ only numerically.

In a recent paper[1], Mullay presented a new set of group electronegativity values, χ_G. His criteria for comparison were the ι values of Inamoto and Masuda[2,3] and the σ_χ values of Taft et al[4], both believed to represent inductive (through-bond) effects. No attempt was made to correlate these χ_G values with σ_I because it is generally accepted[5] that these latter values represent field (through-space) effects. Such a correlation is attempted here, and the results are discussed in terms of the statistical analyses and the variability of individual data points.

Of the groups listed by Mullay in his Tables III and IV, twenty had readily available σ_I values. They are found in Table I, where the σ_I values are those given in the compilation of Gordon and Ford[6], which was used because it is both comprehensive and critical.

Figure 1 contains plots of both ι and χ_G vs σ_I. Both lines give comparable scatter. The statistics are particularly revealing. For ι, the points fit the equation

$$\iota = (0.98 \pm 0.22)\ \sigma_I + (2.22 \pm 0.06); \qquad (1)$$

for 20 data points, the correlation coefficient of 0.72103 indicates a statistical significance of >99.95%. Similarly, χ_G fit the equation

$$\chi_G = (2.57 \pm 0.55)\ \sigma_I + (2.55 \pm 0.17); \qquad (2)$$

here, the correlation coefficient of 0.73213 also indicates a statistical significance of >99.95%. Thus, both ι and χ_G are related to σ_I by the highest statistical significance while equation (1) reveals that ι is, in fact, σ_I plus a constant. These correlations bring into question any distinction between ι, χ_G, etc., and σ_I other than numeric.

Several previous attempts have been made to plot inductive vs field values. One, by Inamoto and Masuda in Figure 6 of their original paper[1], suffered from the fact that older values of ι were used. These values ultimately evolved[3b] into the values found in Table I.

TABLE I
GROUP INDUCTIVE AND FIELD VALUES

Group	ι	χ_G	σ_I
CH_3	2.14	2.32	-0.05
$CHCH_2$	2.34	2.56	0.15
CN	2.61	3.46	0.56
CF_3	2.47	3.10	0.42
NH_2	2.47	3.15	0.10
$N(CH_3)_2$	2.48	3.24	0.10
NO_2	2.75	4.08	0.63
OH	2.79	3.97	0.25
OCH_3	2.82	4.03	0.26
SH	2.17	2.42	0.23
CH_2CH_3	2.15	2.35	-0.05
$CH(CH_3)_2$	2.15	2.38	-0.07
$C(CH_3)_3$	2.16	2.41	-0.07
CHO	2.39	2.89	0.31
$COCH_3$	2.39	2.93	0.28
CO_2CH_3	2.37	3.16	0.30
$CONH_2$	2.30	3.06	0.21
$OCOCH_3$	2.80	4.18	0.39
F	3.10	4.73	0.52
SCH_3	2.16	2.46	0.19

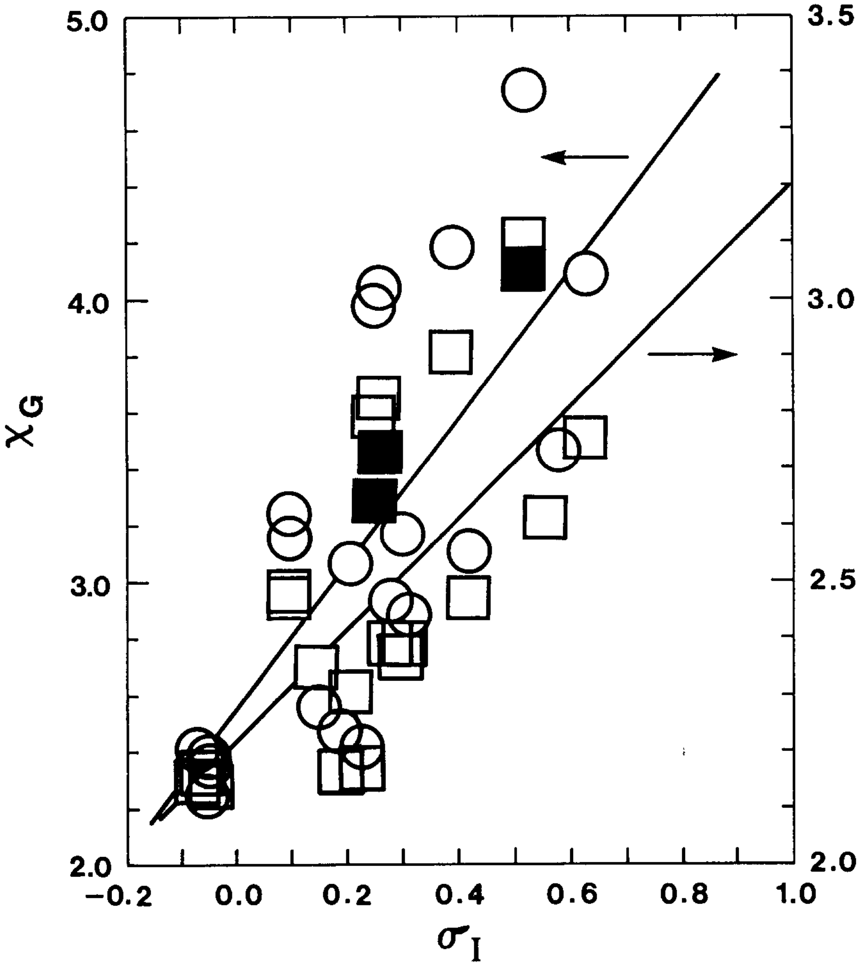
A second attempt was made by Taft et al in Figure 5 of their paper[4]. Although no statistics are available, their plot of σ_I vs σ_χ appears to be linear with high scatter, as noted by the authors. No plots of ι vs σ_χ were given, so comparisons are not possible.

The plot of ι vs σ_I, in Figure 1, shows good linearity except for F, OH and OCH_3. However, in the latest ι compilation[3b], the authors give three methods for evaluating ι, all of which give reasonably close values. The values listed and used are those of method 1, based on group electronegativities. Those for methods 2 and 3, based, respectively, on bond ionicities and group dipole moments, give lower values, lying up to 1.5 units closer to the line in Figure 1, and are indicated by shaded points. Had they been used here, the scatter would have been substantially reduced.

In passing, it should be noted that a plot of χ_G vs ι, not shown but similar to Figure 2 of reference 1, fit the equation

$$\chi_G = (2.55 \pm 0.11)\ \iota - (3.08 \pm 0.27); \qquad (3)$$

the correlation coefficient of 0.98334 indicates a statistical significance of >99.95%. This equation disagrees with equation (12) of Mullay[1], which is written as $\iota = 2.42\chi_G - 2.77$. However, an inspection of his Figure 2, a plot



1. A plot of ι(O) and χ_G(□) vs σ_I for twenty groups. The shaded points indicate alternate values of ι and are discussed in the text.

of ι vs χ_G, indicates both a slope of less than unity and a positive intercept. It would thus appear that an inadvertent error has been made in Mullay's equation (12), which is corrected merely by exchanging his ι and χ_G.

In conclusion, statistical comparisons among ι, χ_G and σ_I indicate they differ only numerically. If it is accepted that both ι and χ_G represent inductive effects, so must σ_I; any data interpreted as indicating otherwise may have to be reexamined.

REFERENCES

1. Mullay, J., J. Am. Chem. Soc., 1985, 107, 7271
2. Inamoto, N.; Masuda, S., Tetrahedron Lett., 1977, 3287
3. Inamoto, N.; Masuda, S., Chem. Lett., 1982 (a) 1003, (b) 1007
4. Marriott, S.; Reynolds, W.F.; Taft, R.W.; Topsom, R.O., J. Org. Chem., 1984, 49, 959
5. Reynolds, W.F., J. Chem. Soc., Perkin II, 1980, 985
6. Gordon, A.J.; Ford, R.A., "The Chemist's Companion", Wiley- Interscience: New York, 1972, p. 153.

(Received in USA 19 May 1986)