Group Electronegativity and Polar Substituent Constants

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The relationship between polar substituent constants (σ^*) and group electronegativity values (X) calculated by the method of phosphoryl absorption frequencies has been examined. The relations $X = 0.37\sigma^* + 2.06$ and $X = 0.26\sigma^* + 2.30$; $r = 0.88$ were obtained. From these relationships, the group electronegativity of 44 organic groups was calculated and compared with values obtained by various other methods wherever possible.

It was originally felt that electronegativity was a fixed property of atoms.[2] However, several workers have recently suggested that the electronegativity of an atom is not invariant but depends upon its environment in a molecule.[3-7] Clifford has shown that group electronegativity values may be obtained by simply averaging the individual electronegativity values of the atoms comprising the group.[8]

It has long been postulated that the Taft σ^* values are a function of electronegativity.[9] Jaffé, *et. al.*, obtained one relationship for various fluorinated methyls, and another relationship for various chlorinated methyls, but neither hydrogen nor the monobromo- or monoiodomethyls fell on either of these two curves.[7b] Other values of group electronegativity have been obtained empirically from infrared,[10] solubility,[8] basicity and coupling potential,[11] and nmr data,[12] but no relationship between these values and σ^* has been established.

Recently,[13] Huheey has presented a method for calculating group electronegativity by assuming variable electronegativity of the central atom in the group and equalization of electronegativity in all bonds.[15] This method of electronegativity equalization has most recently led to an equation relating σ^* and the charge (δ) induced on the carbethoxy group as calculated from group electronegativity.[14] This manuscript also presents a general empirical relationship between group electronegativity (X) obtained from phosphoryl absorption frequencies, and polar substituent constants (σ^*).

Methods.—The electronegativities of various substituent groups were obtained by substituting the phosphoryl-stretching frequencies obtained by Griffin[16] into both the Bell equation (eq 1) and the Robinson equation (eq 2) relating ΣX with phosphoryl absorption frequencies.[10b,d]

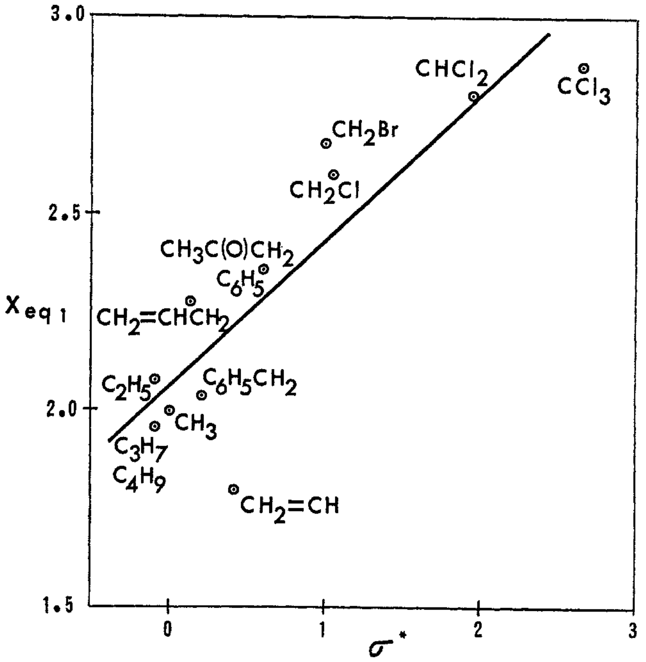

Figure 1.—Plot of $X_{eq\,1}$ vs. σ^*.

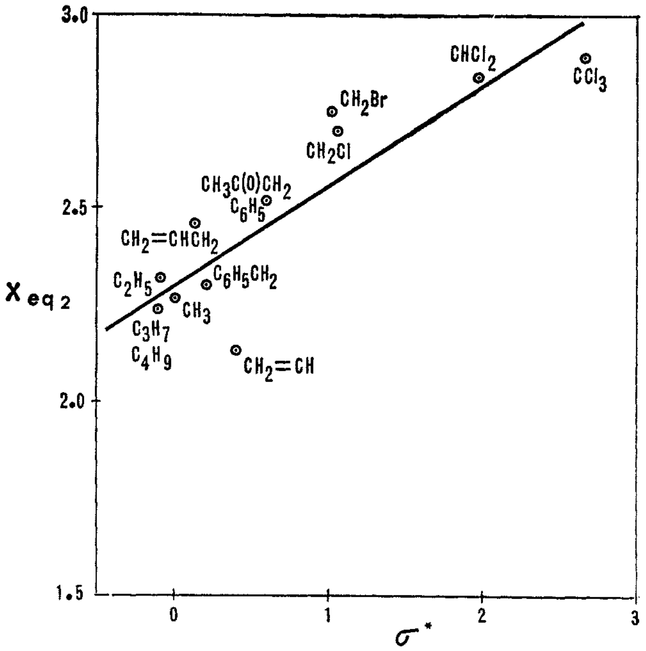

Figure 2.—Plot of $X_{eq\,2}$ vs. σ^*.

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[2] L. Pauling and D. M. Yost, *Proc. Natl. Acad. Sci. U. S.*, **14**, 414 (1932); L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[3] A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

[4] R. T. Sanderson, *J. Chem. Educ.*, **31**, 2 (1945); "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960.

[5] H. O. Pritchard and F. H. Sumner, *Proc. Roy. Soc.* (London), **A235**, 136 (1956).

[6] R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).

[7] (a) J. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962); (b) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, **85**, 148 (1963); (c) J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, **67**, 1501 (1963).

[8] A. F. Clifford, *ibid.*, **63**, 1227 (1959).

[9] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729, 3120 (1952).

[10] (a) R. E. Kagarise, *ibid.*, **77**, 1377 (1955); (b) J. V. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *ibid.*, **76**, 5185 (1954); (c) J. K. Wilmshurst, *J. Chem. Phys.*, **28**, 733 (1958), and earlier papers; (d) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

[11] D. H. McDaniel and A. Yingst, *J. Am. Chem. Soc.*, **86**, 1334 (1964).

[12] B. P. Dailey and H. N. Shoolery, *ibid.*, **77**, 3977 (1955).

[13] It should be noted that this paper was first submitted for publication before the work of Huheey appeared in print.[14]

[14] J. E. Huheey, *J. Org. Chem.*, **31**, 2365 (1966).

[15] (a) J. E. Huheey, *J. Phys. Chem.*, **68**, 3073 (1964); (b) *ibid.*, **69**, 3284 (1965); (c) *ibid.*, **70**, 2086 (1966).

[16] C. E. Griffin, *Chem. Ind.* (London), 1058 (1960).

TABLE I

CALCULATION OF GROUP ELECTRONEGATIVITY (X) FROM EQ 1 AND EQ 2

R	λ (μ)	λ (cm^{-1})	σ^*	$X_{\text{eq }1}$	$X_{\text{eq }2}$
CH_3	8.05	1242	0.00	2.00	2.27
C_2H_5	8.03	1245	−0.10	2.08	2.32
n-C_3H_7	8.06	1241	−0.11	1.96	2.24
n-C_4H_9	8.06	1241	−0.13	1.96	2.24
$CH_2{=}CH$	8.10	1234	0.40	1.80	2.13
$CH_2{=}CHCH_2$	7.98	1253	0.13	2.28	2.46
$C_6H_5CH_2$	8.04	1244	0.21	2.04	2.30
C_6H_5	7.96	1256	0.60	2.36	2.52
CH_2Cl	7.90	1266	1.05	2.60	2.70
$CHCl_2$	7.85	1274	1.94	2.80	2.84
CCl_3	7.83	1277	2.65	2.88	2.89
CH_2Br	7.88	1269	1.00	2.68	2.75
$CH_3C(O)CH_2$	7.96	1256	0.60	2.36	2.52

$$\lambda\ (\mu) = (39.96 - \Sigma X)/3.995 \qquad (1)$$

$$\lambda\ (\text{cm}^{-1}) = 55.9\Sigma X + 791 \qquad (2)$$

The compounds used were diethylalkyl or -aryl phosphonates of the type $(C_2H_5O)_2P(O)R$. Once ΣX is obtained it is a simple matter to subtract the electronegativity due to the two ethoxy groups, thus leaving the electronegativity of the R group (X). The ethoxy group was assigned an electronegativity of 2.90, so that $\Sigma X - 5.80 = X$. The results along with the corresponding phosphoryl-absorption frequencies and σ^* values are shown in Table I.[17]

TABLE II

COMPARISON OF CALCULATED AND LITERATURE ELECTRONEGATIVITY VALUES

No.	Group	σ^*	$X_{\text{eq }1}$	$X_{\text{eq }2}$	$X_H{}^a$	X_{other}
1	F_2CH	2.05	2.82	2.84	3.00	2.81,[b] 2.94,[b] 3.12[c]
2	$CH_3OC(O)$	2.00	2.80	2.82	2.94	2.54[d]
3	$(CH_3)_3N^+CH_2$	1.90	2.76	2.79	2.62	
4	$CH_3C(O)$	1.65	2.67	2.73	2.69	2.59[d]
5	CH_3O	1.46	2.60	2.68	2.68	2.48,[e] 2.52,[c] 2.83[d]
6	O_2NCH_2	1.40	2.58	2.66		
7	C_2H_5O	1.35	2.56	2.65	2.53	2.41,[e] 2.44,[c] 2.83[d]
8	$C_6H_5C{\equiv}C$	1.35	2.56	2.65	2.61	
9	$CH_3S(O_2)CH_2$	1.32	2.55	2.64	2.86	
10	$NCCH_2$	1.30	2.54	2.64	2.96	
11	FCH_2	1.10	2.47	2.59	2.61	2.39,[b] 2.61,[b] 2.70[c]
12	$HOC(O)CH_2$	1.05	2.45	2.57	2.98	
13	CF_3CH_2	0.92	2.40	2.54	2.90	2.36,[b] 3.01[c]
14	ICH_2	0.85	2.38	2.52	2.37	2.08,[b] 2.36,[c] 2.38[b]
15	$C_6H_5OCH_2$	0.85	2.37	2.52	2.58	
16	$C_6H_5C(OH)H$	0.76	2.34	2.50	2.59	
17	$C_2H_5OC(O)CH_2$	0.71	2.32	2.48		
18	$(CH_3)_2N$	0.65	2.30	2.47	2.40	2.37,[c] 3.00[d]
19	$HOCH_2$	0.55	2.26	2.44	2.74	2.08,[d] 2.52[c]
20	CH_3OCH_2	0.54	2.25	2.44	2.52	
21	$O_2NCH_2CH_2$	0.50	2.24	2.43	3.07	
22	H	0.49	2.24	2.43	2.20	2.20[b]
23	$C_6H_5CH{=}CH$	0.41	2.21	2.41	2.48	
24	$(C_6H_5)_2CH$	0.40	2.21	2.40	2.48	
25	$ClCH_2CH_2$	0.38	2.20	2.40	2.49	2.07[b]
26	$CH_3CH{=}CH$	0.36	2.19	2.39	2.37	
27	$CF_3CH_2CH_2$	0.32	2.18	2.38	2.70	
28	$CH_3CH{=}CHCH_2$	0.13	2.11	2.33	2.45	
29	$CF_3CH_2CH_2CH_2$	0.12	2.10	2.33	2.60	
30	$C_6H_5C(CH_3)H$	0.11	2.10	2.33	2.42	
31	$C_6H_5CH_2CH_2$	0.08	2.09	2.32	2.42	
32	$C_6H_5C(C_2H_5)H$	0.04	2.07	2.31	2.40	
33	$C_6H_5CH_2CH_2CH_2$	0.02	2.06	2.30	2.40	
34	c-$C_6H_{11}CH_2$	−0.06	2.04	2.28	2.29	
35	i-C_4H_9	−0.12	2.01	2.27	2.29	
36	c-C_6H_{11}	−0.15	2.00	2.26	2.29	2.60[d]
37	$(CH_3)_3CCH_2$	−0.16	2.00	2.26	2.29	
38	i-C_3H_7	−0.19	1.99	2.25	2.28	2.29[c]
39	c-C_5H_9	−0.20	1.99	2.25	2.29	
40	sec-C_4H_9	−0.21	1.98	2.25	2.29	
41	$(C_2H_5)_2CH$	−0.22	1.98	2.24	2.29	
42	$(CH_3)_3SiCH_2$	−0.26	1.96	2.23	2.33	
43	$(CH_3)_3C(CH_3)CH$	−0.28	1.96	2.23	2.29	
44	t-C_4H_9	−0.30	1.95	2.22	2.29	2.29[c]

[a] Calculated inherent electronegativity (a) in Pauling units.[15] [b] Calculated by Jaffé.[7] [c] Calculated by the method of Clifford[8] using electronegativity values of Jaffé.[7] [d] Calculated by the method of Bell.[10b] [e] Calculated by the method of Sanderson.[4]

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[17] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966.

Results and Discussion

The least-squares linear regression equations of X vs. σ^*, as shown in Figures 1 and 2, gave eq 3 and 4.

$$X_{\mathrm{eq}\ 1} = 0.37\sigma^* + 2.06 \qquad (3)$$

$$X_{\mathrm{eq}\ 2} = 0.26\sigma^* + 2.30 \qquad (4)$$

The standard deviation from regression ($S_{X\cdot\sigma^*}$) was 0.17 for eq 3 and 0.12 for eq 4. The Student "t" test gave $t = 6.18$ and 6.24, respectively, both of which have $p < 0.01$ for 11 degrees of freedom. The correlation coefficient is 0.88 for both equations.

It can be seen from Table II that, in almost all cases, agreement with previous electronegativity values is quite good. Of the 44 groups examined only groups 10, 12, 13, 19, 21, 27, and 29 differ significantly ($p < 0.05$) from X_H values and of these only groups 12, 13, and 21 differ significantly from X_H at the 0.01 level. Table II also illustrates the principle that the group electronegativity is mainly due to the contribution of the first atom and to a smaller extent from the contribution of the second atom. Huheey has made note of the fact that the assumption of perfect electronegativity equalization gives equal "weight" to all atoms in the group, but, in reality, the electronegativity of a group is always influenced most by the atom which links the group to the remainder of the molecule.[15c] With this in mind, it is felt that the X_H values of groups 21, 27, and 29 are most likely overestimates and that the X_H values of groups 10, 12, 13, and 19 may also be somewhat on the high side.

Although Robinson's criticism[10d] of the work of Bell, *et. al.*,[10b] is probably correct, and his omission of the fluorine compounds from the equation is justified, the result is really not significant in the determination of group electronegativity. The $X_{\mathrm{eq}\ 2}$ values only differ from the $X_{\mathrm{eq}\ 1}$ values by 10% for the very low σ^* values and are nearly identical for σ^* values >1.50. Thus it is felt that either eq 3 or eq 4 can be used to give a good estimate of group electronegativity.

The Reduction of Methyl Viologen by Cyanohydrin Anions

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In order to elucidate the mechanism of oxidation of cyanohydrin anions, the character of the methyl viologen reduction by these anions was investigated. The over-all rate of the reaction was governed by the rate of formation of the cyanohydrin anions ($k_1 = 4 \times 10^3$ l. mole^{-1} min^{-1}). A stoichiometric ratio of two methyl viologen cation radicals was produced per molecule of cyanohydrin consumed. It is concluded that p-cyano- and p-nitrobenzaldehydecyanohydrin anions reduce methyl viologen to the radical cation by a one-electron-transfer process.

In a previous report,[1] it was shown that the cyanohydrin anions of p-nitrobenzaldehyde and p-cyanobenzaldehyde reduce 1,2-dinitrobenzene to o-nitrophenylhydroxylamine. The possibility existed that the reduction is effected *via* hydride transfer, as in the case of the Cannizzaro reaction,[2] or by electron transfer to yield radical anions as exemplified by the numerous citations of Russell,[3,4] or alternatively that a transfer of a hydrogen atom may be involved in the reduction step. Attempts to study the cyanohydrin anions *per se* were unsuccessful. The cyanohydrin anion of p-nitrobenzaldehyde collapses to form a variety of azo-, azoxy-, and nitrosobenzoic acids,[5] while the cyanohydrin anion of p-cyanobenzaldehyde yields the corresponding benzoin derivative which, in the presence of the cyanohydrin anions, is reduced to the deoxybenzoin with the concomitant formation of p-cyanobenzoic acid and an unidentified viscous oil.[6] Since the cyanohydrin anions are not amenable to direct measurement, it was considered feasible to study their reaction with known one electron acceptors, *e.g.*, the viologens,[7] *via* an interception technique.

The viologen (I) upon interception of an electron, is converted to the highly colored and stable free radical (III), which may be measured spectrophotometrically. The reaction is depicted in Scheme I.

This report deals with the evidence in support of Scheme I and the significance thereof.

Results and Discussion

Table I summarizes the results of semiquantitative experiments run to determine the reaction in alkaline solution of p-nitro- and p-cyanobenzaldehyde with methyl viologen and 2,3,5-triphenyltetrazolium chloride (TTC) in the presence and absence of cyanide ion. The reaction of other reductants is also included. It can be seen that while ascorbate and benzoin anions reduce methyl viologen and TTC directly, p-nitro- and p-cyanobenzaldehyde in alkaline medium require cyanide ion for the reduction.

A kinetic study of the reaction of p-cyanobenzaldehyde, cyanide ion, and methyl viologen revealed first-order dependance on p-cyanobenzaldehyde and cyanide ion and a zero-order dependance on methyl viologen (Table II), similar to what was observed in the reaction of p-nitrobenzaldehyde, cyanide, and 1,2-dinitrobenzene.[1] The rate was measured by following the change with time of the absorbance at 600 mμ. The molar absorptivity of the methyl viologen radical cation, used to calculate the rates in Table II, was 1×10^4.[7] The reaction kinetics are in consonance with Scheme I, where $k_1 >> k_{-1}$ and less than k_2, k_3, and k_4

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[1] D. N. Kramer and G. G. Guilbault, *J. Org. Chem.*, **31**, 1103 (1966).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., Inc., New York, N. Y., 1940, pp 350–352.

[3] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4143, 4155 (1962).

[4] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

[5] G. Heller, *Ber.*, **46**, 285 (1913).

[6] J. H. Ashley, H. J. Buber, A. Ewins, G. Newberry, and A. D. Self, *J. Chem. Soc.*, 114 (1942).

[7] E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5527 (1964).