THE PRINCIPLE OF ELECTRONEGATIVITY EQUALIZATION

II- FORCE CONSTANTS

by

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In the preceeding paper of this series we have shown how it is possible, by taking into account the hybridization effect and the charge effect, to calculate the effective electronegativities of bonded atoms. The present paper will be concerned with the relations between the effective electronegativities of the atoms and the vibrational stretching force constante.

Gordy [1], considering that in a vibratory bond A-B both A and B are displaced with respect to the center of gravity of the bonding electron cloud, established the empirical relationship:

$$k = a N \left\{ \frac{X_A(0) \cdot X_B(0)}{d^2} \right\}^{3/4} + b \qquad (1)$$

in which k is the force constant of the bond A-B, N is the bond order, $X_A(0)$ and $X_B(0)$ are the electronegativities of atoms A and B, d is the average inter-nuclear distance in the vibrational ground-state, and a and b are two constants. If k is measured in 10^5 dynes.cm^{-1} and d in Angstrom unities, a and b have the values 1.67 and 0.30, respectively. Gordy's equation holds surprisingly well for a great number of bonds although no satisfactory theoretical interpretation of it has been given [1,2]. Since the electronegativities of the bonded atoms differ from those of the free atoms we must expect that a different relationship should exist between the strength of a bond A-B and the equalized electronegativities.

Both the bond dissociation energy, D(A-B), and the stretching force constant, k(A-B) measures the strength of a bond A-B. The first one, however, involves many terms besides the attraction of the bonding electrons by the bonded atoms: π-bonding, valence shell - valence shell repulsion, inner shells repulsion, and the change in hybridization during bond formation or dissociation[3]. Even if we limit ourselves to A-H bonds, all the repulsive terms and also π-bond formation are absent, but the change in hybridization (re-arrangement energy) during bond dissociation persists. The force constant of A-H bonds, corrected for unharmocities,

measures the bond strength for very small perturbations, and we can expect that a simple relatioship should hold between the attraction of the bonded atoms for the bonding electrons, given by the effective electronegativities, and the force constants of A-H bonds.

We have identified electronegativity as an electrostatic potential and, as the inter-nuclear distance varies the acting force must vary with d^{-2}. Hence we must expect that a linear relation should hold between the force constant and the ratio of the effective electronegativity to the square of the inter-nuclear distance. Graph 1 shows a plot of k(A-H) (in 10^5 dynes.cm^{-1}) versus X/d^2 (X in eV/6.3 and d in Angstrom unities; X is the effective electronegativity [4] calculated by the method described in the preceeding paper of this series), and Table I shows the data from which the graph was constructed. The following equation fits the curve of graph 1:

$$k(A-H) = 2.36 \left\{ \frac{X}{d^2} \right\} + 0.95 \qquad (2)$$

Table II shows the values of k(A-H) calculated from equation (2), and the observed values of k(A-H). The average percent deviation from the experimental values is 1.5%; Gordy's equation gives for these same force constants an average percent deviation of 3.0%, but it must be said that equation (1) applies for a great number of bonds, whereas equation (2) applies only for A-H bonds.

Equation (2) can be used to estimate the hybridization

state of the bonding orbitals in A-H bonds. For example,
$k = 3.39 \times 10^5$ dynes.cm^{-1} for phosphine, PH_3, according to Gamo[5].
From equation (2), and knowing the inter-nuclear distance $\underline{d}$, we
compute the value of X, hence the value of X(O) for phosphorus.
The figure obtained corresponds to 4% $\underline{s}$-character of the bonding
orbital of the phosphorus atom in PH_3. This agrees well with the
value obtained from bond angle data, 5% $\underline{s}$-character [6].

Still in this connection it must be pointed out that the
force constants of the O-H bonds in H_2O and OH fit the curve of
graph 1 only if we assume that in H_2O the oxygen atom uses hybrid
$\underline{sp}^3$ orbitals whereas in OH the oxygen atom uses pure $\underline{p}$ orbitals [7].

Two points merit comments. The first one refers to the
electronegativity of silicon. Heath and Linnett [8] obtained the
value of k(Si-H) for the molecule SiH_4 as 3.04×10^5 dynes.cm^{-1},
whereas from equation (2) and using the $\underline{sp}^3$ electronegativity of
silicon as given by Pritchard and Skinner [9] one obtains
3.44×10^5 dynes.cm^{-1}. We think that this discrepancy is one
argument more against the extremely high value (2.44) of the $\underline{sp}^3$
electronegativity of silicon given by those authors. It must be
pointed out that this high value falls outside the limits of the
$\underline{sp}^3$ electronegativity of silicon given by twelve different methods
and summarized by Rochow and Allred [10].

The other point is the following: it has been recognised
for a long time that the F-F bond in F_2, as well as other single
bonds between first period atoms, N-N, O-O, etc, are exceedingly
weak when compared with the single bonds of the corresponding
heavier atoms (such as Cl-Cl, P-P, S-S, etc.). On the other hand

the first period atoms form very strong multiple bonds, such as O-O, N N, etc., whereas heavy atoms form only very weak multiple bonds. To interpret this fact, Mulliken[11] suggested that it is not the F-F, N-N, etc. bonds which are abnormally weak, but instead that it is the Cl-Cl, Br-Br, S-S, etc., bonds which are abnormally strong.

To limit our discussion to the halogen molecules, Mulliken suggested that in F_2 the F-F bond is a pure single bond but that in the other halogen molecules the X-X bonds involve a certain ammount of π-bonding, by the use of the vacant $\underline{d}$ orbitals of the atoms of chlorine, bromine, and iodine. In other words, in the molecules X_2 there is some $\underline{p},\underline{d}$ hybridization and the hybrid $\underline{p},\underline{d}$ orbitals are used for π-bonding. F_2 is an exception because the $2\underline{p} \rightarrow 3\underline{d}$ transition energy is too high to be compensated by the extra π-bond energy[12]. Now, equation (2) was established on the assumption that in the A-H bonds there are not either valence shell - valence shell repulsive terms nor attractive terms such as those arising from π-bonding. Since in the molecules X_2 repulsive terms are certainly present, and these weaken the bonds, we should expected that by applying equation (2) to these molecules we will obtain consistently higher values for k(X-X) than the experimental ones. The results are shown in Table III and we can see that only for F_2 is this expectation fullfilled. For Cl_2 and Br_2 the calculated values are smaller than the experimental values, and for I_2 there is a good agreement between the two values. This fact suggests that the Cl-Cl and Br-Br bonds are abnormally strong and that in the I-I bond the strong repulsive terms of such heavy atoms just counterbalence the extra π-bond energy.

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BIBLIOGRAPHY AND NOTES

1. W. GORDY, J. Chem. Phys., 14, 305 (1946).
2. A. D. WALSH, Proc. Roy. Soc., A-207, 13 (1951).
3. K. S. PITZER, J. Am. Chem. Soc., 70, 2140 (1948); R.S.MULLIKEN, Ibid., 72, 4493 (1950).
4. R. S. MULLIKEN, J. Chem. Phys., 2, 782 (1934).
5. I. GAMO, Compte. Rendus, 239, 1478 (1954).
6. From the formula $a^2 = \cos\theta/(\cos\theta - 1)$, as given by T.P.DAS, and E. L. HALM, "Nuclear Quadrupole Resonance Spectroscopy", Academic Press, New York, 1958, p. 142.
7. Although the sp^3 electronegativity of oxygen differs greatly from the p-electronegativity, the effective electronegativities of oxygen in H_2O and OH are nearly the same because the ΔX^- values of an sp^3 oxygen is also much larger.
8. D. F. HEATH, and J. W. LINNETT, Trans. Faraday Soc., 46, 137 (1950).
9. H. O. PRITCHARD, and H. A. SKINNER, Chem. Revs., 55, 745 (1955).
10. E. G. ROCHOW, and A. L. ALLRED, J. Inorg. Nucl. Chem., 5, 269 (1958).
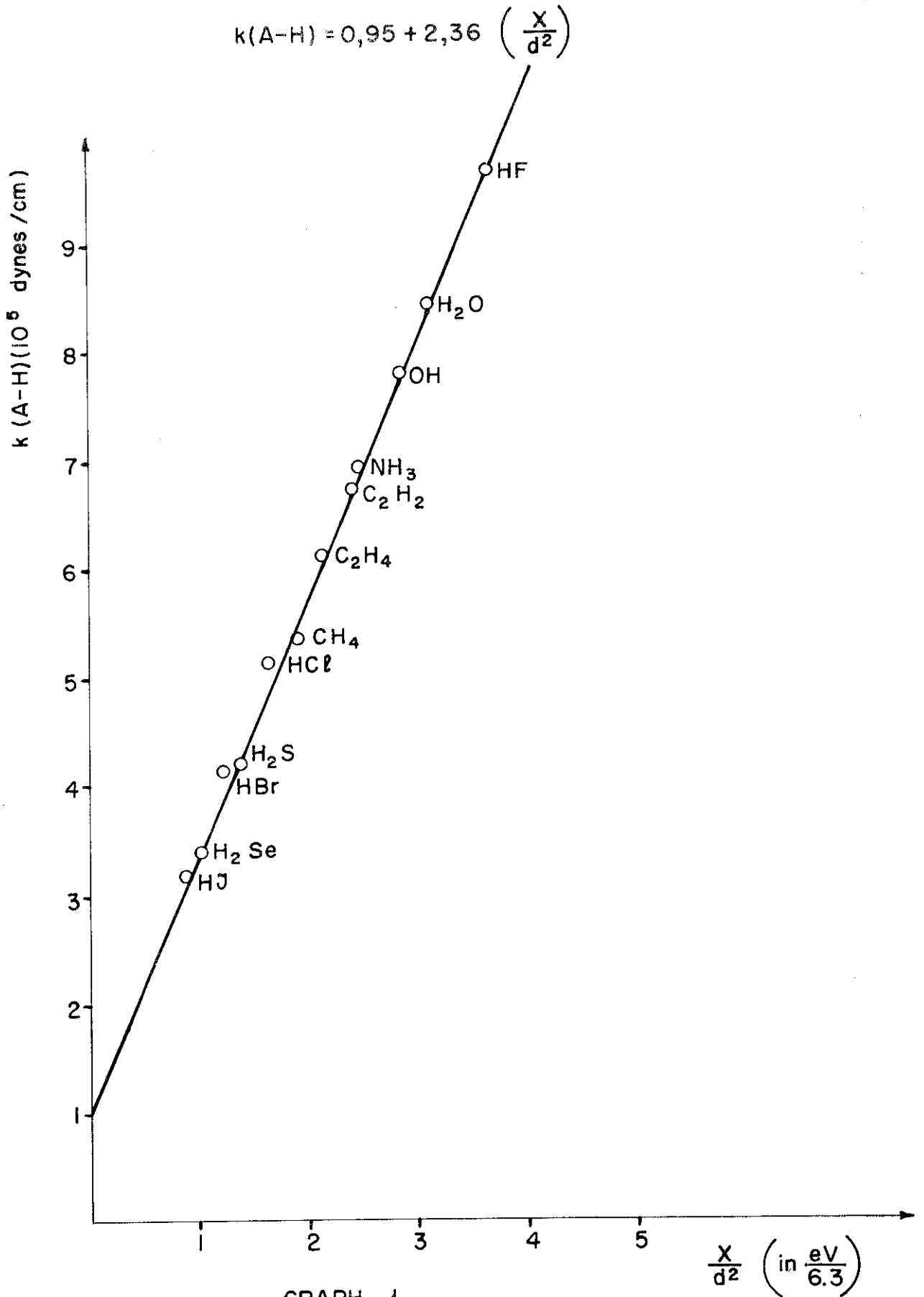11. R. S. MULLIKEN, J. Am. Chem. Soc., 77, 884 (1955).

$$k(A-H) = 0,95 + 2,36 \left(\frac{X}{d^2} \right)$$

GRAPH 1

T A B L E   I

Molecule	H-A-H Bond angle	Hybridization state of A	X	d^2	X/d^2	k(A-H)
HF	180°	p	3.13	0.84	3.72	9.66
HCl	180°	p	2.70	1.62	1.67	5.16
HBr	180°	p	2.53	1.99	1.27	4.12
HI	180°	p	2.42	2.59	0.93	3.14
OH	180°	p	2.72	0.94	2.89	7.79
H_2O	104° 27'	sp^3	2.89	0.92	3.14	8.43
H_2S	92° 6'	10% s	2.50	1.77	1.42	4.20
H_2Se	91°	p	2.26	2.16	1.05	3.37
NH_3	107° 20'	sp^3	2.59	1.03	2.51	6.94[a]
CH_4	tetrah.	sp^3	2.36	1.21	1.95	5.39
C_2H_4	120°	sp^2	2.48	1.15	2.16	6.13
C_2H_2	180°	sp	2.77	1.12	2.47	6.75[b]

X - Effective electronegativity in eV/6.3, calculated by the method described in the preceeding paper.

k(A-H) - Experimental values in 10^5 dynes.cm^{-1}.

d - Average internuclear distance in the vibrational ground-state in Angstrom unities.

Values of k(A-H) and d given by T. L. Cottrell, "The Strengths of the Chemical Bonds", Butterworths, London, 2nd. edition, 1958, except in the cases a and b.

a - S. Sundaram, F. Suszek, and F. F. Cleveland, J. Chem. Phys., 32, 251 (1960).

b - F. L. Keller, A. H. Nielsen, and W. H. Shaffer, Mem. Soc. Roy. Liege, 18, 480 (1957).

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T A B L E   II

Molecule	k(A-H) observed	k(A-H) calculated	k(calc) from k(obs) % deviation
HF	9.66	9.72	0.6 %
HCl	5.16	4.89	5.2 %
HBr	4.12	3.95	4.1 %
HI	3.14	3.14	0.0 %
OH	7.79	7.79	0.0 %
H_2O	8.43	8.36	0.8 %
H_2S	4.20	4.30	2.4 %
H_2Se	3.37	3.42	1.5 %
NH_3	6.94	6.87	1.0 %
CH_4	5.39	5.45	1.1 %
C_2H_4	6.13	6.05	1.3 %
C_2H_2	6.75	6.78	0.4 %

Average percent deviation: 1.5 %

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T A B L E   III

Molecule	X(O)	X/d^2	k(X-X) calculated	k(X-X) observed
F_2	3.91	1.89	5.40	4.45
Cl_2	3.00	0.75	2.74	3.29
Br_2	2.76	0.53	2.20	2.46
I_2	2.56	0.35	1.78	1.72

k(X-X) in 10^5 dynes.cm^{-1}.

X(O) in eV/6.3.

d   in Angstrom unities.