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Berkeley, California

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William L. Jolly

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Electron Repulsions in Compounds of Nitrogen, Oxygen and Fluorine

By William L. Jolly

Department of Chemistry, and Inorganic Materials Research Division
of the Lawrence Radiation Laboratory, University of California,
Berkeley, California

By comparisons of bond energies and bond lengths, it is shown that single bonds of the type N-X, O-X, and F-X (where X is a very electronegative element) are abnormally weak, and that this weakening increases with increasing electronegativity of the atom X. It is pointed out that this bond weakening may be attributed to repulsions between the bonding electrons and lone-pair electrons.

Introduction

The abnormally low N-N, O-O, and F-F bond energies in the molecules N_2H_4, H_2O_2, and F_2 are usually explained in terms of the repulsions between the non-bonding valence electrons on adjacent atoms.[1,2] It has recently been shown that, in compounds of the type H_3M-X (where M = C, Si, or Ge), the M-H bonding electrons are repelled by the X atoms, and this repulsion increases as the X atoms are made more electronegative.[3] It therefore seemed reasonable that in single bonds of the type N-X, O-X, and F-X, the repulsions between the X atoms and the lone-pair electrons on the adjacent atoms should become very important for highly electronegative X atoms. We contend that N-X, O-X, and F-X bonds (where X is very electronegative) are weaker than one would predict from a comparison with other bonds and that this weakening increases with increasing electronegativity of the X atom. In this paper we shall show that two methods for measuring bond weakening bear out this contention. One method involves a comparison of the usual thermochemical bond energies; the other involves a comparison of bond lengths. We shall also discuss the possibility that an important cause of bond weakening is the repulsion between lone pair electrons and the bonding electrons.

Comparison of Bond Energies

If we exclude bonds between electronegative atoms and fluorine, oxygen, and nitrogen, it is usually found that, if E(M-A) > E(M-B), then E(N-A) > E(N-B). (Here E refers to the bond energy[4] —— a quantity not necessarily equal to the bond dissociation energy.) Consequently a plot of M-X bond energies against the corresponding N-X bond energies yields a fairly smooth curve, in some cases a straight line. We show two plots of this type in Figure 1, in which both H-X and Cl-X bond energies are plotted against C-X bond energies. We believe the points for X = Si fall off the curves because of the tendency for silicon to form double bonds to electronegative elements and because of hyperconjugation in the case of the Si-CH_3 bond. The H-H bond is weak because of poor overlap of the 1s orbitals.[5]

When F-X, O-X and N-X bond energies are plotted against C-X bond energies (Figures 2-4), the points corresponding to very electronegative X atoms fall below the expected curve. In accordance with our contention that bond weakening increases with increasing electronegativity of the X atom, the points for X = F show the greatest discrepancies, the points for X = O show the next greatest discrepancies, and the points for X = Cl and N show relatively small discrepancies.

Comparison of Bond Lengths

Huggins[5] has shown that abnormally weak bonds are abnormally long. Therefore, we expect to find that bonds of the type F-X, O-X, and N-X (where X is a very electronegative element) are abnormally long (when compared with the sums of the appropriate covalent radii as determined from other bond lengths), and that this bond lengthening increases with increasing electronegativity of X. Schomaker and Stevenson[6] have in effect shown that this is true by showing that the lengths of bonds of this type may be calculated by using abnormally long covalent radii for F, O and N and by subtracting a term proportional to the difference in electronegativity of the bonded atoms. However, their method predicts much too short bond lengths for the C-Cl and C-Br bonds.

We find that if we use the normal single bond covalent radii as tabulated by Pauling[7] (except we take 0.59 A as the radius for fluorine, so as to obtain the correct C-F distance), and add a correction term to the F-X, O-X and N-X bond lengths in order to account for electron repulsions, we can predict bond lengths as well as by means of the Schomaker-Stevenson equation. Our correction, in Angstrom units, is $+ 0.07(X_x - 2.5)$, where X_x is the

electronegativity of X. Two corrections are added when X = F, O, or N. No correction is to be applied when $X_x < 2.5$. In Table I we have tabulated twenty bond lengths[8] together with the differences between the actual bond lengths and those calculated using the Pauling radii, the Schomaker-Stevenson equation, and our method.

It will be noted that, except for the Schomaker-Stevenson method, an enormous discrepancy occurs for the case of the H-H bond. (In the Schomaker-Stevenson method, the radius for hydrogen is taken as half the H_2 bond length.) If we exclude this bond (which there is good reason to consider is anomalously long)[9], the average deviation for our method becomes ±.015A as compared with ±.016A for the Schomaker-Stevenson method. None of the methods yields good results for bonds to second- and third-row elements such as Si, P and As without special corrections to account for double-bonding between these elements and electronegative elements.

Table I.

Experimental and Calculated Bond Lengths

Bond	r_{obs}	$r_{obs}-r_p$	$r_{obs}-r_{ss}$	$r_{obs}-r_{calc}$
FF	1.42	0.24	0.00	0.03
OF	1.42	.17	.01	.00
OO	1.48	.16	.00	.02
NF	1.36	.07	.01	-.07
NO	1.44	.08	.01	-.02
NN	1.46	.06	.00	-.01
ClF	1.63	.05	.02	+.01
ClO	1.70	.05	.01	.01
NCl	1.75	.06	.03	.02
BrF	1.76	.02	.02	.00
CF	1.36	.00	.02	.00
CCl	1.77	.01	.05	.01
CBr	1.94	.03	.06	.03
CO	1.43	.00	.01	.00
CN	1.47	.00	.01	.00
HF	.92	.03	.01	.03
HCl	1.27	-.02	-.01	-.02
NH	1.01	+.01	-.01	+.01
OH	.96	.00	-.02	.00
HH	.74	.14	.00	.14
Average Δ:		±.060	±.016	±.022

Discussion

The results, although confirming our expectations regarding the repulsive effects of highly electronegative atoms, do not tell us the principal cause of these repulsive effects. The repulsive effect of a bonded atom is generally attributed to the valence electrons of the atom other than those in the weakened bond itself. We wish to suggest that an appreciable fraction of the repulsive effect of a bonded atom arises from the electrons in the bond. The shorter the bond, the higher the density of bonding electrons and the stronger the repulsion. In the following paragraphs, we show that the bonding in Cl_2 and F_2 may be qualitatively discussed from this point of view, and thus, it is hoped, we point up a significant problem for theoreticians.

Consider the Cl_2 molecule, whose bond energy is normal. Here the atoms are large enough that there is little repulsion between the non-bonding electrons and the bonding electrons. The bond is probably formed by the overlap of essentially pure p atomic orbitals,[10] and the non-bonding electrons may be thought of as existing in sp^2 hybrid orbitals lying in a plane perpendicular to the molecular axis. Very little hybridization of the bonding atomic orbital occurs because the promotional energy required would not be compensated for

by the improved overlap of the orbitals.

In F_2, the bonding would be completely analogous to that in Cl_2 were it not for the fact that the atoms are so small that there is strong repulsion between the non-bonding and bonding electrons. The non-bonding electrons bend back away from the bond (with a consequent shift of s character to the bonding orbital). Considerable energy is required to accomplish this rehybridization of the atomic orbitals, and consequently the bond energy is much less than it would be in the absence of electron repulsions.

Acknowledgment

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References

(1) K. S. Pitzer, J. Am. Chem. Soc., 70, 2140 (1948).

(2) L. Pauling, "The Nature of the Chemical Bond," 3rd edition, Cornell University Press, 1960, pp. 142-144.

(3) W. L. Jolly, in press.

(4) For a table of bond energies and methods of calculation see Ref. 2, pp. 83-87.

(5) In molecular H_2 the 1s orbitals of the atoms cannot overlap strongly because of the spherical symmetry of the orbitals and the proton-proton repulsion. However, when a hydrogen atom forms a bond to an atom which offers a highly directional bonding orbital (e.g., sp^3), the hydrogen atom can "immerse itself" in the other atom's bonding orbital, and thus very strong orbital overlap can be achieved.

(6) M. Huggins, J. Am. Chem. Soc., 75, 4123 (1953).

(7) V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc., 63, 37 (1941).

(8) Reference 2, pp. 224 and 227.

(9) Special Publication No. 11, "Interatomic Distances," L. E. Sutton, editor, The Chemical Society, London, 1958.

(10) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N.Y., 1953, p. 510.

Figure Captions

Figure 1. H-X and Cl-X bond energies vs. C-X bond energies.

Figure 2. F-X bond energies vs. C-X bond energies.

Figure 3. O-X bond energies vs. C-X bond energies.

Figure 4. N-X bond energies vs. C-X bond energies.

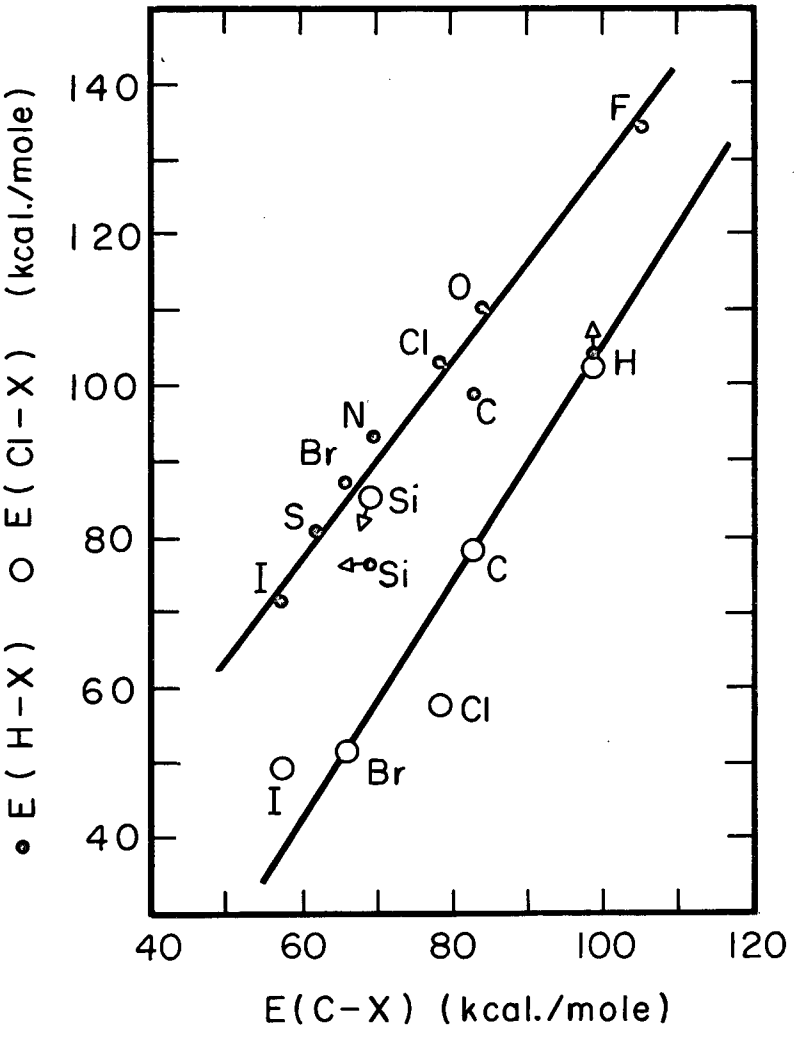

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Fig. 1

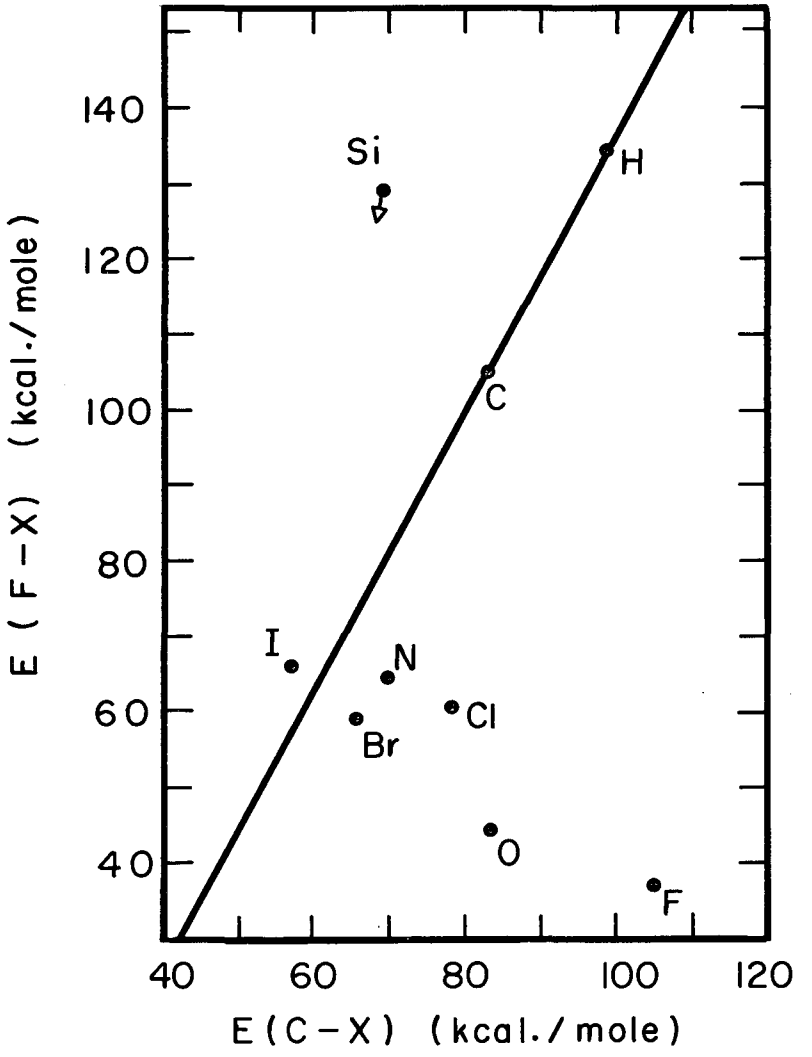

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Fig. 2

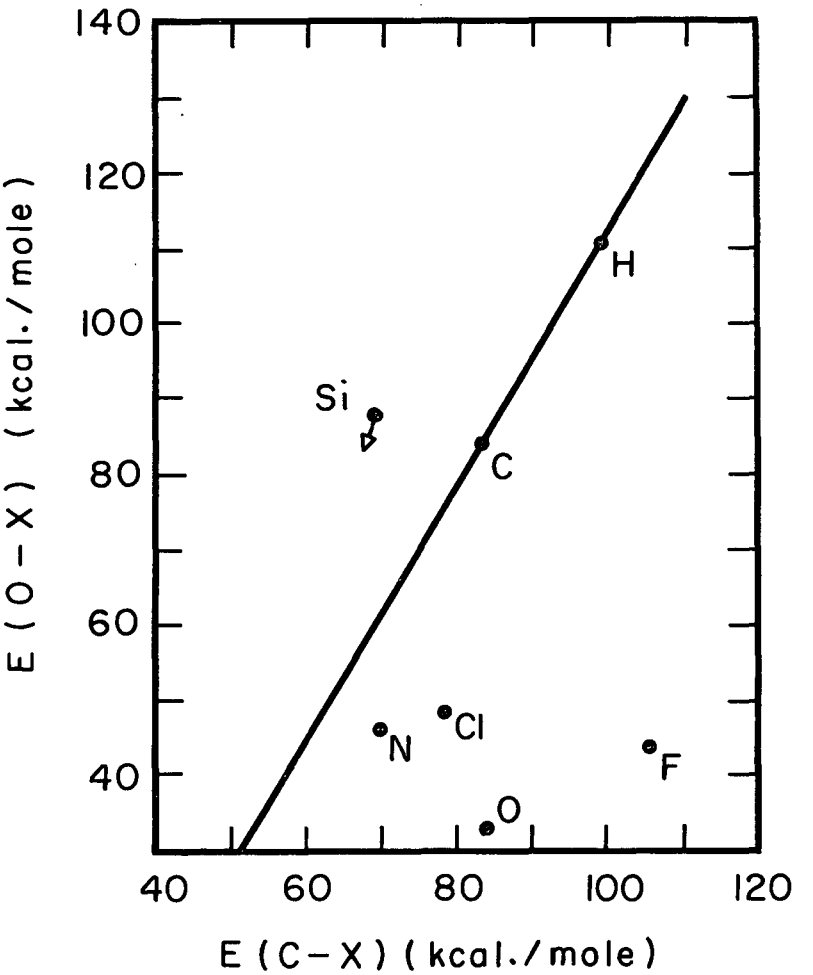

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Fig. 3

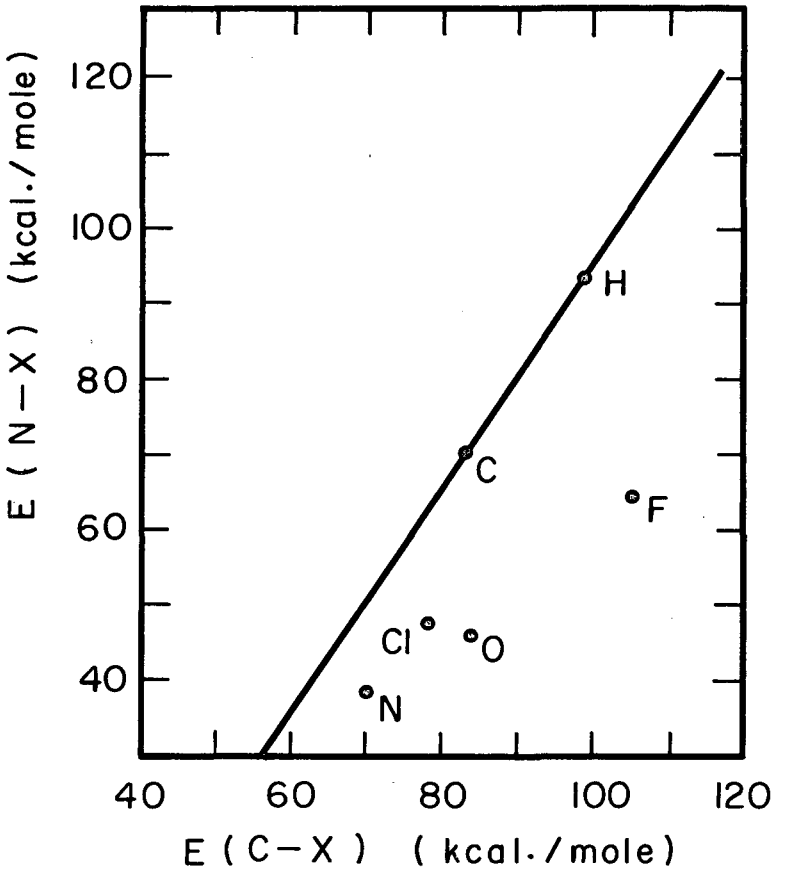

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Fig. 4

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