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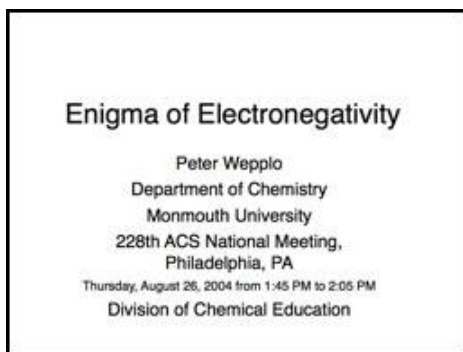
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Electronegativity

Background

Organic chemists know that tertiary carbocations are more stable. Similarly, every organic chemist knows iodides are better leaving groups and more reactive than bromides and in turn chlorides, and much more than fluorides. The notion that fluoride has more anionic character in a reaction in which the slow step is formation of an anion is counterintuitive. They also know that tertiary butyllithium is extremely reactive and methyllithium is more stable. Simply, if we were making electronegativity arguments, iodine would be more electronegative than fluoride and hydrogen is more electronegative than carbon. The electronegativity should follow the acidity of HI (pKa ~-10), a stronger acid than HF (pKa ~3), and hydrogen (pKa ~35, NaH) a stronger acid than methane (pKa ~50).

When I began teaching and to teach electronegativity, I was uncomfortable with how it fit in with real chemistry, with reactions, with reactivity and with reaction products. I looked up Pauling's 1932 paper on electronegativity. Pauling knew that some compounds were more stable than expected. Fluorine had the greatest difference. He thought the increase in stability of fluoride and other atoms was due to Coulombic attraction of the ions. In 1932, that idea was ingenious. The electronegativity values matched what chemists knew, $F > O > N > C$. The electronegativity values must be correct, right?

When I read the paper, I knew some compounds did not match the profile asserted by Pauling. Pauling stated that Coulombic attraction can only **increase** bond strength and at its lowest, **no effect**. Didn't the metal hydrides disprove the electronegativity principle? This had been considered the paradox of electronegativity. To resolve this problem, Pauling squared the terms in order to change the sign of the effect on bond strength. The decrease in bond strength was treated as though it increased it. I am not the first to note this.

What I am not aware of is anyone disagreeing with Pauling's conclusion with his rationale for increased bond strength and to suggest a reason why fluoride might have strong bonds and metal hydrides might be weaker. Below is a synopsis of a presentation from the Philadelphia ACS meeting in 2004.

Since then, I have removed some aspects of the argument to make it less controversial (I hope). The basic ideas are present in Chapter 1 of "The Language of Organic Chemistry" but with no mention of electronegativity.


I was also prompted to write this in response to some student discussion about electronegativity.

From my ACS presentation, below are relevant slides.

What were the signs of the times?

1932 - Linus Pauling and Electronegativity

- Scientists did not have a comprehensive model for atomic structure
- Periodic table and chemical properties well understood
 - Alkali metals
 - Halogens
 - Nobel gasses
 - Atomic properties
- 1931 Paper on chemical bond
- 1932 Paper on Electronegativity



This is the data Pauling used.

Thermodynamic Calculation

- Followed postulate that normal covalent bond energies are additive
 - $A : B = 1/2 (A : A + B : B)$
- Pauling estimated each atom's contribution to bond energy
- Polar bonds are greater in bond energy than predicted

	kJ/mol	B.E./2
H-H	436	218
F-F	160	80
H-F	Calc	298
	Expt	550
	Diff	272

This is Pauling's hypothesis for this energy difference.

Premise of Electronegativity

- Pauling hypothesized that Coulombic forces may be responsible for the energy difference
- Hence if the postulate of additivity is correct, the difference between the actual bond energy and the predicted must be zero or positive, and the greater the ionic character of the bond, the greater will be the difference.*

$$A-B \longleftrightarrow A^{\oplus} B^{\ominus}$$

$$E_{Total} = E_{Covalent} + E_{Coulombic}$$

*Pauling, L., *Journal of the American Chemical Society* 54, 3570 (1932)

A comparison of electronegativity values and pKa values.

Paradox of Electronegativity

- Pauling Electronegativity

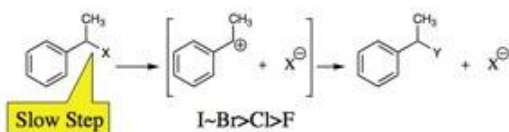
- General agreement with increase in electronegative effect across periodic table
- May overly simplify atomic properties with molecular properties
- Doesn't predict HX acids

	E_{neg}	pKa
HF	4.0	3.2
HCl	3.0	-7
HBr	2.8	-9
HI	2.5	-10

Maybe the H-X bond is anomalous. Lets look at the carbon-halogen bond.

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect

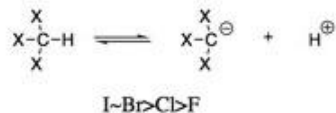


Hine, J., Burski, N.W., Hine, M., Langford, P.B.: J. Am. Chem. Soc.; 79, 1406 (1957).

Lets look at the effect if we move the electronegative element more distant to the bond that changes. Now, it should not be a function of the actual bond and its length, but an inductive effect.

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect
 - Alpha effect - trihalomethanes
 - Will electronegative elements stabilize carbanions?



Hine, J., Burski, N.W., Hine, M., Langford, P.B.: J. Am. Chem. Soc.; 79, 1406 (1957).

Lets look at moving the electronegative atom further away, such as the acetic acids. This is an often cited example and see, fluorine is more acidic because it is more electronegative.

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect
 - Alpha effect - trihalomethanes
 - Acetic acids

$$\text{R-CH}_2\overset{\text{O}}{\parallel}\text{C-O-H} \rightleftharpoons \text{R-CH}_2\overset{\text{O}}{\parallel}\text{C-O}^\ominus + \text{H}^\oplus$$

R	E _{neg}	pKa
H	2.1	4.76
F	3.98	2.59
Cl	3.16	2.87
Br	2.96	2.90
I	2.66	3.18

Oh, oh, nitroacetic is a stronger acid than fluoroacetic acid and hydroxyacetic and thiolacetic acid are out of order and less than all of the haloacetic acids. Propionic acid is also less acidic. Looks like another anomaly.

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect
 - Alpha effect - trihalomethanes
 - Acetic acids

$$\text{R-CH}_2\overset{\text{O}}{\parallel}\text{C-O-H} \rightleftharpoons \text{R-CH}_2\overset{\text{O}}{\parallel}\text{C-O}^\ominus + \text{H}^\oplus$$

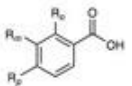
R	E _{neg}	pKa	R	E _{neg}	pKa
H	2.1	4.76	CH ₃	2.55	4.87
F	3.98	2.59	O ₂ N	3.04	1.48
Cl	3.16	2.87	HO	3.44	3.83
Br	2.96	2.90	HS	2.68	3.68
I	2.66	3.18			

Lets look at the effect on other bonds, obviously I am selectively picking my data, right?

Oh no, not more bad data. Note, methyl is **more** electronwithdrawing here. (Probably because it is ortho and interferes with the interaction of the carboxylate group and the aromatic ring.) Fluorine is the least electronegative atom (again).

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect
 - Alpha effect
 - Acetic acids
- Other compounds
 - Benzoic acids

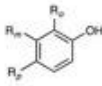


E _{neg}	R	Ro	Rm	Rp
2.1	H	4.204	4.204	4.204
2.55	CH ₃	3.91	4.25	4.37
3.98	F	3.27	3.86	4.25
3.16	Cl	2.90	3.84	4.00
2.96	Br	2.85	3.81	3.96
2.66	I	2.86	3.87	4.00

More bad data. Anyone care to look an anilines? I skipped them, but the effect is the same, fluorine is the least electronegative and carbon less than hydrogen.

Electronegativity Effects

- HX
- Other bond effects?
 - C-X bond effect
 - Alpha effect
 - Beta effect
- Other compounds
 - Benzoic acids
 - Phenols



E_{avg}	R	R_o	R_m	R_p
2.1	H	9.99	9.99	9.99
2.55	CH ₃	10.26	10.29	10.09
3.98	F	9.89	8.73	9.29
3.16	Cl	9.41	8.56	9.13
2.96	Br	9.37	8.45	9.03
2.66	I	9.33	8.51	9.03

Lets look at lithium hydride. Remember the difference must be positive?

Paradox of Electronegativity

- Pauling Electronegativity
 - Alkali metal hydrides
 - Less stable than predicted

	B.E/2	kJ/mol
H-H	218	436
Li	55	110
Li-H	Calc	273
	Expt	238
	Diff	-35

It must be positive because lithium (positive) and hydride (negative) must be **attractive** in an ionic bond according to the electronegativity theory.

Paradox of Electronegativity

- Pauling Electronegativity
 - Alkali metal hydrides
 - Less stable than predicted
 - The principle of Coulombic attraction violated
 - "the predicted [difference] must be zero or positive"

$$\text{Li}-\text{H} \longleftrightarrow \text{Li}^{\oplus} + \text{H}^{\ominus}$$

$$E_{\text{Total}} = E_{\text{Covalent}} + E_{\text{Coulombic}}$$


Coulombic attraction should **increase** bond strength.

*Pauling, L., *Journal of the American Chemical Society* 54, 3570 (1932)

Is it possible that Pauling was wrong?

Paradox of Electronegativity

- **Electronegativity**
 - Follows core atom effect
 - Not a simple atomic property
 - Inconsistencies in data
 - Pauling's formulation doubtful
 - Increased bond strength not due to ionic character
- **Questions**
 - Explanation for increased bond strength
 - 'Correct' electronegativity order



Is this a good model for atomic structure? Aren't there multiple charges present? Is the separation of ionic charges a good model to predict bond strength?

Increased Bond Strength

- Pauling hypothesized that Coulombic forces may be responsible for the energy difference

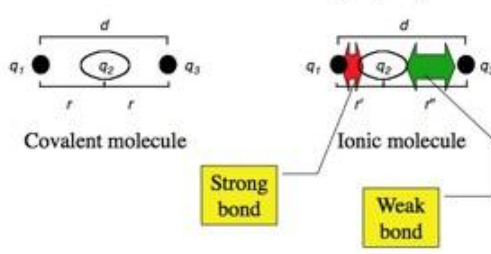
$$A-B \longleftrightarrow A^{\oplus} B^{\ominus}$$

- Q: Is this a good model for atomic structure?

Let me suggest another simple model for bond strength consistent with Coulomb's Law. If nucleus q_1 pulled the bonding electrons q_2 closer to it, those electrons would be held more strongly. Conversely, if the electrons moved away from q_3 , they would be held less tightly. The effect is that q_1 would have a negative charge and q_3 a positive. This is another model for an ionic molecule.

Increased Bond Strength

- Coulomb's Law

$$F = k * \left(\frac{q_1 * q_2}{r^2} \right)$$


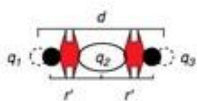
Covalent molecule Ionic molecule

Strong bond Weak bond

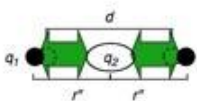
If the ionic bond model were applied to the halides, they should have shorter (stronger) bonds than predicted while the metal hydrides have longer (weaker) bonds than predicted? While it is difficult to find consistent data for different bond lengths, I must leave you to answer that question. The metal hydride bonds lengths appear to be longer, but it depends upon how the data was gathered and whether other bond lengths are determined in the same manner.

Increased Bond Strength

- Coulomb's Law
$$F = k * \left(\frac{q1 * q2}{r^2} \right)$$



Strong bond




Weak bond

Metal hydride bonds are generally longer than HX bonds.

Okay, that may work for the halogens, but carbon is more electronegative than hydrogen, right?

Organic Chemistry Electronegativity Order

- Core charge effect
 - F>O>N>C
 - I>Br>Cl>F
 - HX
 - Solvolysis data
 - S>O
- Carbon vs Hydrogen?



Lets go back to the examples. We know methyl carbocation is less stable than a tertiary and methyl anion is more stable then tertiary.

Organic Chemistry Electronegativity Order

- Carbon vs Hydrogen?
 - H>C
 - Cation stability

$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}^{\oplus}-\text{H} \end{array}$$

➡

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}^{\oplus}-\text{CH}_3 \end{array}$$

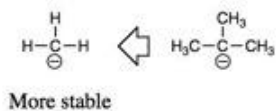
More stable

Organic Chemistry Electronegativity Order

- Carbon vs Hydrogen?

- H>C

- Cation stability
- Carbanion stability



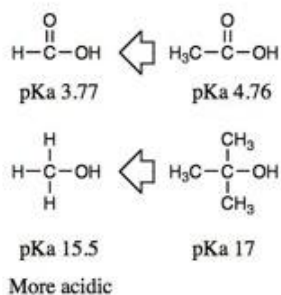
Uncle?

Organic Chemistry Electronegativity Order

- Carbon vs Hydrogen?

- H>C

- Cation stability
- Carbanion stability
- Acidity

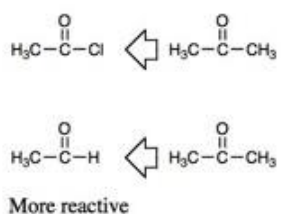


Organic Chemistry Electronegativity Order

- Carbon vs Hydrogen?

- H>C

- Cation stability
- Carbanion stability
- Acidity
- Carbonyl reactivity



Summary

- Desirable to have consistent cause and effect
- Pauling's interpretation of bond strength may have been premature
- Possible to create a more consistent electronegativity order from organic chemistry data
- What about the other 100+ papers on electronegativity?



This is just the first part of my thoughts on atoms and bonding. I confess many of the other ideas are equally avant-garde. It is my objective to make those ideas the subject matter of another book.
PW

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