A Consideration of the Concepts of Relative Electronegativity

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The concept of relative electronegativity, as applied to organic chemistry, was first observed by Markovnikov in 1870 while studying the addition reactions of the olefin bond. At that time he formulated his observations into a rule which has since come to bear his name. An English translation of his original statement reads: "When an unsymmetrically constituted hydrocarbon combines with a halogen acid, the halogen of the acid adds on to the less hydrogenated carbon atom, that is, to the carbon atom which is under the influence of the other carbon atoms" (1). Somewhat later he stated that the addition of halogen acid to "vinyl chloride, chloropropylene, and other analogs" takes place so that the halogen of the acid becomes bonded to the carbon atom that already supports a halogen atom.

Wagner and Saytzeff observed that in the addition of halogen acids to olefins of the type $R{\cdot}HC{:}CH{\cdot}R'$, where R′ is lighter than R, the halogen of the acid becomes bonded to the carbon atom which is linked to the lighter alkyl radical (2).

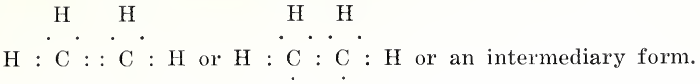
In 1899 Michael evidenced a better understanding of this phenomena in his statement that "every system tends toward that state whereby the maximum chemical neutralization is reached." To show that this applied to addition reactions of the olefin bond he treated propylene with both iodochloride and bromochloride to give the results indicated by the equations (3):

$CH_3{\cdot}HC{:}CH_2 + I{\cdot}Cl \rightarrow CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}I$ (3 parts) $+ CH_3{\cdot}CHI{\cdot}CH_2{\cdot}Cl$ (1 part), and $CH_3{\cdot}HC{:}CH_2 + Br{\cdot}Cl \rightarrow CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}Br$ (7 parts) $+$ $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}Cl$ (5 parts).

The results clearly indicate that some kind of an electrical effect is involved, for the three-to-one ratio in the first equation becomes a seven-to-five ratio in the second equation.

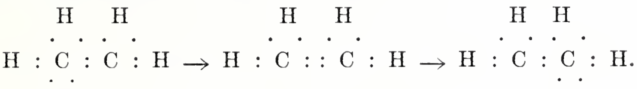
During the next forty years a number of workers contributed to progress in this field. Ipatieff observed that temperature, solvent, and other factors effect the ratio of end products of any given reaction (4). Lapworth proposed his theory of "alternate latent polarities"(5) and both Biach and Cuy cited physical data pertaining to melting points, heats of crystallizations, heats of combustions, and molecular volumes in confirmation of this postulate (6, 7). These workers visualized the organic molecule as being composed of a chain of carbon atoms in which there is a decided tendency for alternate atoms to be positively charged with the corresponding negative charges on the intervening atoms. It has been argued, however, that the concept is not valid since no corresponding irregularity is observed with respect to the boiling points, refractive indices, molecular volumes, and other properties of these same homologous series (8, 9).

Lewis, in 1923, postulated that the olefin bond is best represented by:



$$H : \overset{\overset{H}{\cdot\,\cdot}}{C} :: \overset{\overset{H}{\cdot\,\cdot}}{C} : H \text{ or } H : \underset{\cdot}{\overset{\overset{H}{\cdot\,\cdot}}{C}} : \underset{\cdot}{\overset{\overset{H}{\cdot\,\cdot}}{C}} : H \text{ or an intermediary form.}$$

Carothers (1924) extended the Lewis formulation to include two active and one inactive form, as represented by (10):



$$H : \underset{\cdot\,\cdot}{\overset{\overset{H}{\cdot\,\cdot}}{C}} : \overset{\overset{H}{\cdot\,\cdot}}{C} : H \rightarrow H : \overset{\overset{H}{\cdot\,\cdot}}{C} :: \overset{\overset{H}{\cdot\,\cdot}}{C} : H \rightarrow H : \overset{\overset{H}{\cdot\,\cdot}}{C} : \underset{\cdot\,\cdot}{\overset{\overset{H}{\cdot\,\cdot}}{C}} : H.$$

active form inactive form active form

Stieglitz recognized the phenomena of relative electronegativity for he employed "the direction of the addition of a halogen acid as the criterion for the determination of the relative electronegativities of the two carbon atoms joined by a double bond" (11). This idea has been extended by Lucas (12), by Kharasch (13), by Ingold (14), and others, but each has used his own method for assigning relative electronegativities. With these contending concepts in the literature, Pauling developed his Electronegativity Map which offers another method of assigning relative electronegativities to the constituent atoms of an organic molecule (15).

There are, consequently, at the present writing, four viewpoints that must receive some consideration, namely, that of the doubters, that of Lucas, that of Kharasch, and that of one of the authors of this paper.

Referring to the doubters, it must be conceded that there are organic chemists who still cling to the belief that (a) relative electronegativity does not manifest itself in organic compounds, or (b) its application is beyond the realm of feasibility. Aside from the directive addition to unsymmetrical olefin bonds, the development of the Pauling Electronegativity Map, if it is correctly interpreted, seems to afford ample evidence for the Electronegativity concept as a working hypothesis in organic chemistry. Experimental data points more and more to the belief that the essential difference between an organic reaction and an analogous inorganic reaction is one of degree rather than one of type. Sodium hydroxide, for example, reacts with hydrochloric acid to give sodium ion, chloride ion, and water, and sodium acetylide reacts similarly to give sodium ion, chloride ion, and acetylene. The essential difference between the sodium-chlorine bond in the former and the sodium-carbon bond in the latter is one of degree rather than one of type.

The Lucas (16) postulate differs from the original Lapworth (17) concept in that the former considers an inductive effect in lieu of the alternate polarity concept, as illustrated by:

$$H \; :\underset{\underset{H}{\cdot\,\cdot}}{\overset{\overset{H}{\cdot\,\cdot}}{C}} \; :\underset{\underset{H}{\cdot\,\cdot}}{\overset{\overset{H}{\cdot\,\cdot}}{C}} \; :\overset{\overset{O}{:\,:}}{C} \; :O \; :H \quad \text{versus} \quad H:\underset{\underset{H}{\cdot\,\cdot}}{\overset{\overset{H}{\cdot\,\cdot}}{C}} \; :\underset{\underset{H}{\cdot\,\cdot}}{\overset{\overset{H}{\cdot\,\cdot}}{C}}: \overset{\overset{O}{:\,:}}{C} \; :O: \; H, \text{ or}$$

$CH_3{}^+$ $-CH_2{}^+$ $-CO^+$ $-OH$ versus $CH_3{}^+$ $-CH_2{}^-$ $^+CO^+$ $-OH$.

inductive effect of Lucas *alternate polarity effect of Lapworth*

Lucas arrives at the relative electronegativity of the various radicals by a consideration of the ionization constants of the acids, alcohols, phenols, and other compounds. There is, for example, a decrease in acidity in passing from acetic through propionic to butyric acid, hence Lucas argues that the order of decreasing electronegativity is methyl, ethyl, propyl. This system of measuring relative electronegativity is independent of the addition of halogen acids to olefin bonds and has, consequently, value that must not be disposed of too lightly. The idea of a lop-sided electrical charge, on the other hand, seems to be opposed to the general tendency of an electrical charge to be distributed symmetrically. The electrons tend to form completed octets and to take up positions at the corners of an imaginary tetrahedron because by so doing they are distributing themselves symmetrically about the atom concerned. To the writers it seems unlikely, in view of our present concepts of the behavior of electricity, that one side of an atom will carry a positive charge whereas the other side will carry a negative charge. It should be pointed out, moreover, that the Lucas postulate like the Lapworth concept is dependent on key atoms or groups for the direction of the displacement, but the former theory does provide a means for deciding between two or more contending forces.

Kharasch has developed the Stieglitz concept by actually using the addition of halogen acids to olefins to determine the relative electronegativities of the residues concerned. In the addition, for example, of H·X to R·HC:CH·R′ the direction of addition is noted and it is reasoned that the X group becomes bonded to the more electropositive carbon atom of the olefin pair hence the alkyl residue attached to this particular carbon atom is more strongly electronegative or electron attracting than is the other substituent alkyl group. If, to cite a specific case, 2-pentene is treated with hydrogen chloride, the principal reaction takes the course:

$$CH_3{\cdot}CH_2{\cdot}HC{:}CH{\cdot}CH_3 + HCl \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3.$$

This is interpreted by Kharasch as meaning that the methyl group is more electronegative than is the ethyl group, and on this basis, by varying the substituents, he has built up a relative electronegativity series (18). The main disadvantage of this system, as the authors of this paper see it, are that (1) one is reasoning in a circle, and (2) the system has definite limitations. That is, one uses a reaction to test out the relative electronegativities of the radicals and then cites the directive addition as proof for the relative electronegativities of the carbon atoms concerned. In the second place, the system deals only with compounds containing olefinic linkages and hence limits its application to a very small field of organic chemistry.

The system proposed by one of us is a direct application of the Electronegativity Map of Linus Pauling. This table, in an *abridged* form for the purpose of this discussion, places the H atom at 2.1, the carbon, sulfur, and iodine atoms at 2.5, the bromine atom at 2.8, the nitrogen and chlorine atoms at 3.0, and the oxygen atom at 3.5, as indicated by Table I:

TABLE I. Abridged Form of the Pauling Electronegativity Map, Expressed in Volt Electrons

1.0	1.5	2.0	2.5	3.0	3.5	4.0
+ ←						→ −
		H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
			S 2.5	Cl 3.0		
				Br 2.8		
			I 2.5			

From this map it is seen that the hydrogen atom lies on the metallic or electropositive side of the carbon atom, whereas the bromine, nitrogen, chlorine, oxygen, and fluorine atoms lie to the nonmetallic or electronegative side of the carbon atom. It is observed, furthermore, that a quantitative relationship is indicated, that is, the difference between a hydrogen atom and a carbon atom is 0.4 volt electrons whereas the differences between a carbon atom and a bromine, nitrogen, chlorine, oxygen, and fluorine atoms are, respectively, 0.3, 0.5, 0.5, 1.0, and 1.5. This suggests the possibility of regarding the organic molecule as an electrostatic aristocracy, in which each constituent atom is assigned a vote on the basis of its position in the Electronegativity Map. For the sake of simplicity, each of these differences are multiplied by the factor 2.5 so as to give hydrogen a value of +1. With hydrogen at +1, the other important values are: S, 0.0; I, 0.0; Br, –0.75; N, –1.25; Cl, –1.25; and singly bonded O, –2.5. On the assumption that a doubly bonded oxygen atom should have about twice the effect of a singly bonded oxygen atom, it is given a value somewhat less than –5.0.

These values enable one to calculate the relative state of equilibrium between the two extreme forms of an electronic system such as that of propylene and acrylic acid:

$$CH_3^{-}\;{}^{+}HC^{+}_{+}\;{}^{-}_{-}CH_2 \rightleftarrows CH_3^{+}\;{}^{-}HC^{-}_{-}\;{}^{+}_{+}CH_2, \text{ and}$$

$$H_2C^{+}_{+}\;{}^{-}_{-}CH^{-}\;{}^{+}CO^{+}\;{}^{-}OH \rightleftarrows H_2C^{-}_{-}\;{}^{+}_{+}CH^{+}\;{}^{-}CO^{-}\;{}^{-}OH.$$

In the case of propylene, the left hand configuration is favored by five of the substituent hydrogen groupings and opposed by only one, hence it is assigned an R. E. (relative electronegativity) ratio of five to one (5/1). This means that approximately 83% of the life of this molecule is best represented by the formulation shown at the left and only 17% of its time is spent in the form shown at the right. Similarly, for acrylic acid the R. E. ratio, provided we consider only the atoms attached directly to the carbon chain, is eight and one-half to two (8.5/2, that is 5 for doubly bonded oxygen, 2.5 for singly bonded oxygen, and 1 for the *alpha*-hydrogen atom as opposed to 1 each for the two *beta*-hydrogen atoms). This suggests that in addition reactions about 83% of the product should be that in which the negative addend becomes bonded to the *beta*-carbon atom and the remaining 17% should represent the corresponding *alpha* variety.

With respect to olefin addition, the rule has been checked qualitatively against over two hundred cases recorded in the literature with a validity of better than 95%. The rule has, moreover, been checked quantitatively against a limited number of cases, for which quantitative data are available, with a surprising degree of accuracy. In this connection, however, one should not forget that in a series of competing reactions the nature of the end product is determined by both (a) reaction rate, and (b) the comparative stability of the derived compounds.

By regarding the organic molecule, then, as an electrostatic aristocracy in which all of the atoms determine the relative distribution of the electrons, it becomes possible to predict, by the proper assignment of electrostatic votes, the relative electronegativity of each constituent carbon atom and the composite effect of such a distribution of the electrons on the course of any given reaction.

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