# Relative Electronegativity,[1]

## III. An Empirical Rule

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It has been suggested that the student of organic chemistry should learn all the theories of the science and that he should be able to apply them advantageously in the prediction of reactions and the interpretation of data, but that he should never succumb to belief in these fantasies.([1]) Be that as it may, the value of any theory is a direct function of its usefulness. No theory is accepted until it can be shown that it satisfactorily explains a number of phenomena, and no theory survives after it is shown that these phenomena can be explained on a much simpler basis. It is on the basis of utility alone, the validity of the postulate having been checked against over two hundred fifty cases, that the following empirical rule is offered as an aid in the prediction of organic reactions and the interpretation of experimental data.

*By postulating that both the nature and relative positions of the atoms in an organic molecule determine the distribution of the electrons; it becomes possible to predict, by the proper assignment of electrostatic values, the relative electronegativity of each constituent carbon atom and the composite effect of such a distribution of the electrons on the course of a reaction.*

In setting up the electronegativity map (Fig. I), the predicted bond energies for a number of simple bonds have been subtracted from their corresponding experimentally determined values to give a numerical quantity which has been labeled *delta* (Table I). Pauling attributes the existence of these *delta* values, that is, the difference between the actual and the predicted bond energies, to the ionic character of the bond. The square root of these *delta* values, expressed in volt electrons, accordingly, is then taken as the difference in electronegativities of the respective elements.([2])

This concept permits a quantitative evaluation of the qualitative values already afforded by the arrangement of the elements in the periodic table. Any element W that lies below or to the left of an element Y is electropositive with respect to Y. In general, the electronegative character of the elements increases as one passes from the lower left-hand corner of the periodic table toward the upper right-hand corner. The electronegativity map merely enables a quantitative interpretation of these relationships.([6])

If the organic molecule is regarded as a composite of atoms and electrical forces, each of the atoms must be assigned its electrostatic value. These electrostatic values may be determined conveniently by an

[1] Paper I. A Consideration of the Concepts of Relative Electronegativity, Proc. Ind. Acad. Sci., **50**:94 (1941), II. The Historical Development of the Concepts, Proc. Ind. Acad. Sci., **51**:167 (1942).

interpretation of the data given in the electronegativity map.[2] ([6]) From this map it is seen that the hydrogen atom is placed 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 at 3.5. Since most of the substituent groups on a carbon nucleus are normally hydrogen atoms, it seems advisable to make unity represent the difference between the relative electronegativities of the hydrogen atom at 2.1 and the carbon atom at 2.5. If this difference of 0.4 is taken to represent a unit electrostatic value, then the electrostatic value of the other atoms to be considered may be determined by multiplying the difference shown on the map, between their position and that of the carbon atom, by the factor 2.5. The electrostatic value of the bromine atom, for example, is calculated as follows:

$$2.8 - 2.5 = 0.3, \text{ then } 0.3 \times 2.5 = 0.75.$$

In each of these two cases the sign is minus with respect to the carbon atom. The electrostatic values for the other atoms are calculated in an analogous manner and found to be as given in Table II.

TABLE I. Setting up the Electronegativity Map
Energies of Single Bonds

| | |
|---|---|
| C – C, bond . . | 58.6 Kg. calories per mole by experimental determination, |
| Cl–Cl, bond . . | 57.8 Kg. calories per mole by experimental determination, |
| 2) | 116.4 |
| C –Cl, bond . . | 58.2 Kg. calories per mole, calculated value, but |
| C –Cl, bond . . | 66.5 Kg. calories per mole by experimental determination. |

Therefore, *delta* is 8.3 Kg. calories per mole, which value is interpreted to be a direct measure of the ionic character of the carbon-chlorine bond.

By determining a number of *delta* values, extracting the square root and expressing the result in volt electrons, Pauling has developed a quantitative periodic table namely, The Electronegativity Map.

TABLE II. Electrostatic Values,[3] with Hydrogen at 1

| Element considered | H | C | Br | Cl | N | O | :0 |
|---|---|---|---|---|---|---|---|
| R. E. Vote, H-atom at 1 | +1 | 0 | —0.75 | —1.25 | —1.25 | —2.5 | —5 |

If the electronegativity map and this interpretation can be accepted as being approximately correct, it becomes necessary in the application of this new empirical rule to be guided by two postulates, namely, that:

[2] For an abridged form of the Pauling Electronegativity Map see the first paper of this series. Proc. Ind. Acad. Sci. **50**:97. 1941.

[3] The "electrostatic value" is selected as a convenient unit for these comparisons. These units are obtained by multiplying the net difference between the atom concerned and the carbon atom, on the Electronegativity May, by 2.5 so as to give unity for the hydrogen atom. The doubly-bonded oxygen atom is assigned a value of 5.0 (2 x 2.5), which value, presumably, is much too large.

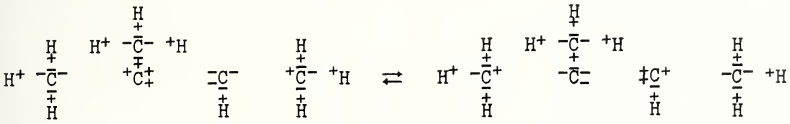
1. The distribution of the electrons in a given molecule is a function of the nature and relative positions of all of the substituent groups of a carbon chain or ring or nucleus, and

2. The properties of organic molecules suggest that the valence electrons *tend to cluster* about alternate carbon atoms, in a chain or ring, so as to produce an alternate polarity effect.

### Addition to Olefin Bonds

The usefulness of the rule in a *qualitative* prediction of addition to an olefin bond may be illustrated by the reaction of hypochlorous acid with 2-methyl-2-butene, which has been studied by Detoeuf, and by the addition of iodine chloride to propene, which has been studied by Michael and by Ingold and Smith.

In setting up the electrostatic formula for 2-methyl-2-butene, the application of postulates 1 and 2 seems to suggest formulas A and B as representing *the two extremes of a type* of a resonating system.



Formula A Formula B

By inspection it may be seen that seven of the electropositive hydrogen atoms in Formula A are bonded to carbon atoms which tend to be completely electronegative, whereas only three electropositive hydrogen atoms are bonded to a carbon atom which bears one or more positive charges and tends to be electropositive. In Formula B, however, only three electropositive hydrogen atoms are bonded to carbon atoms which tend to be slightly electropositive. The ratio of the electrostatic values, therefore, of all of the substituent hydrogen atoms is seven to three (7/3) in favor of Formula A. For convenience, this ratio may be designated as the relative electronegativity (or R. E.) ratio.

If Formula A does represent the electronic configuration of 2-methyl-2-butene, the addition of hypochlorous acid should proceed according to the equation:

$$(CH_3)_2C^+{:}{-}CH.CH_3 + HO{-}.{}^+Cl,\ aq. \rightarrow (CH_3)_2C^+({-}OH).(Cl^+){-}CH.CH_3,$$

but if a more correct picture of the electronic structure of 2-methyl-2-butene is presented by a type of resonance between Formula A and Formula B, and if Formula A is the more correct representation for about 70% of the time and Formula B for only about 30% of the time, the reaction should be formulated as:

$$(CH_3)_2C^+{:}{-}CH.CH_3 + HO{-}.{}^+Cl, aq. \rightarrow (CH_3)_2C{\div}({-}..OH).(Cl^+){-}CH.CH_3,$$

70% yield and

$$(CH_3)_2C{-}{:}{}^+CH.CH_3 + HO{-}.{}^+Cl,\ aq. \rightarrow (CH_3)_2C{-}({}^+Cl).(HO^-){}^+CH.CH_3$$

30% yield.

It is of more than passing interest that Detoeuf(3) studied this reaction both qualitatively and quantitatively, and that he reports 70% of the isomer corresponding to that predicted from Formula A and 30% of the isomer corresponding to that predicted from Formula B.

Propylene may be formulated in terms of these postulates as:

Formula C Formula D

By inspection it is seen that the R.E. ratio for Formula C is 5/1 and that for Formula D is 1/5. If propylene is approximately represented by this type of a resonating system, the addition products should be about 83% of the type predicted from Formula C and only 17% of that predicted from Formula D. Michael,(5) as early as 1892, studied quantitatively the addition of iodine chloride to propylene and obtained the results indicated by the equations:

$CH_3^{-}\ {}^{+}HC_{+}^{+}\ {}^{-}CH_2 + I^{+}\ {}^{-}Cl \longrightarrow CH_3.CHCl.CH_2.I$, 75% yield, and

$CH_3^{+}\ {}^{-}HC_{-}^{-}\ {}^{+}CH_2 + I^{+}\ {}^{-}Cl \longrightarrow CH_3CHI.CH_2Cl$ 25% yield.

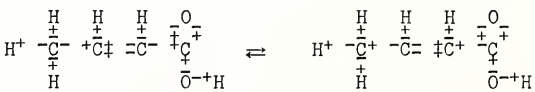
In 1931, Ingold and Smith(4) made a quantitative study of this same addition reaction and reported values of 69% and 31% for the respective isomeric products.

Similarly, Detoeuf(3) studied the addition of hypochlorous acid to 2-hexene and reported yields of 60% of 2-chloro-3-hexanol, whereas relative electronegativity indicates a 50% yield of this isomer.

Over two hundred fifty specific cases of addition have been tabulated and checked qualitatively against this *new empirical rule* with a validity exceeding 95%.

### Addition to Unsaturated Acids and Related Compounds

The application of the rule to the addition reactions of the *alpha-beta* unsaturated acids and related compounds may be illustrated by reference to 2-butenoic acid, which may be formulated as:



Formula E Formula F

If only atoms bonded *directly* to the carbon skeleton are considered, the R.E. ratio is seen to be 11.5/1 in favor of Formula E. Addition reactions should proceed, therefore, so as to give about 92% of the one as compared to 8% of the other isomeric addition product. This particular reaction was studied quantitatively by Ingold and Smith(4) in 1931 who obtained the results indicated by the equations:

$CH_3^- \ {}^+HC^+ \ {}^-CH^+ \ {}^-CO_2H + I^+ \ {}^-Cl \rightarrow CH_3.CHCl.CHI.CO_2H$, 92% yield and

$CH_3^+ \ {}^-HC^- \ {}^+CH^+ \ {}^-CO_2H + I^- \ {}^-Cl \rightarrow CH_3.CHCl.CHI.CO_2H$, 8 % yield.

Reactions of this type involving H.X are usually interpreted by 1, 4— addition, but it must be obvious that iodine chloride cannot add to 2-butenoic acid by any such mechanism. All the additions of H.OX compounds to the *alpha-beta* unsaturated acids are, moreover, in qualitative agreement with this empirical rule. Another interesting case is that of the addition reactions of the acetal of propynal (7) as in the equation:

$$HC\ddagger \ {}^-C^- \ {}^+CH(O{\cdot}Et)_2 + EtO{\cdot}Na/H_2O \rightarrow EtO{\cdot}HC\ddagger = CH^- \ {}^+CH(O{\cdot}Et)_2 + NaOH, \text{ then}$$

$$EtO{\cdot}HC\ddagger = CH^- \ {}^+CH(O{\cdot}Et)_2 + H_2O \rightarrow EtO{\cdot}HC^+({}^-OH){\cdot}(H^+)-CH^-{\cdot}{}^+CH(O{\cdot}Et)_2$$

Considering only the atoms attached *directly* to the carbon nucleus, the R. E. ratio of the acetal of propynal is 5/2.

A number of specific cases of 1, 4— addition have been tabulated and all cases thus far observed are in qualitative agreement with the empirical rule stated at the beginning of this paper.

## General Applicability of the Rule

Cases selected at random from the literature indicate that the rule applies to: (1) all types of addition reactions, (2) condensations, (3) decarboxylations, (4) double decompositions, (5) esterification, (6) rate of ionization, (7) polymerizations, (8) vinylogy, (9) lactol and lactone formation, (10) loss of H.Y from certain types of compounds, (11) rate of oxidation, (12) relative stability, (13) molecular rearrangements, and (14) organic reactions in general.

This empirical rule is not a sure guide, but it does appear to have a high degree of validity. On its usefulness alone, it is offered here as a valuable postulate.

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