Relative Electronegativity IV. An Empirical Rule as a Teaching Tool

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In any discussion dealing with the teaching of organic chemistry, one must not lose sight of the complexity of most organic reactions (2). The reaction of methyl iodide with ethyl iodide, in the presence of sodium in dry ether, may be formulated as:

$$CH_3{\cdot}I + 2Na/(\text{dry ether}) + I{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_3, \text{ propane} + 2NaI.$$

Actually, however, there are two important competing reactions which may be written, namely:

$$CH_3{\cdot}I + 2\ Na/(\text{dry ether}) + I{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_3, \text{ ethane} + 2\ NaI, \text{ and}$$
$$CH_3{\cdot}CH_2{\cdot}I + 2\ Na/(\text{dry ether}) + I{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3, \text{ butane} + 2\ NaI.$$

Although these three equations indicate the principal products that are obtained in this particular reaction, they do not suggest the production of both olefins and higher alkanes as a consequence of a free radical mechanism or its equivalent.

Considering this reaction in terms of a free radical mechanism, a number of things may happen. The sodium atom may abstract the iodine atom from the methyl iodide to give a methyl radical, as:

$$CH_3{\cdot}I + Na/(\text{dry ether}) \rightarrow NaI + CH_3{}^{\circ}, \text{ methyl radical,}$$

or a similar abstraction of the iodine atom from ethyl iodide will yield the ethyl radical in accordance with the equation:

$$CH_3{\cdot}CH_2{\cdot}I + Na/(\text{dry ether}) \rightarrow NaI + CH_3{\cdot}CH_2{}^{\circ}, \text{ ethyl radical.}$$

These free radicals in turn may enter into any one of a number of reactions, as indicated by the following series of equations:

1. $CH_3{}^{\circ} + CH_3{}^{\circ}/(\text{dry ether}) \rightarrow CH_3{\cdot}CH_3$, ethane, or
2. $CH_3{}^{\circ} + CH_3{\cdot}CH_2{}^{\circ}/(\text{dry ether}) \rightarrow CH_3{\cdot}CH_2{\cdot}CH_3$, propane, or
3. $CH_3{\cdot}CH_2{}^{\circ} + CH_3{\cdot}CH_2{}^{\circ}$, by disproportionation $\rightarrow CH_3{\cdot}CH_3 + H_2C{:}CH_2$, or
4. $CH_3{\cdot}CH_2{}^{\circ} + CH_3{\cdot}CH_2{\cdot}CH_3$, by abstraction of H $\rightarrow CH_3{\cdot}CH_3 + CH_3{\cdot}CH_2{\cdot}CH_2{}^{\circ}$, then
5. $CH_3{\cdot}CH_2{\cdot}CH_2{}^{\circ} + CH_3{\cdot}CH_2{}^{\circ} \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, pentane, or
6. $CH_3{\cdot}CH_2{\cdot}CH_2{}^{\circ} + CH_3{\cdot}CH_2{\cdot}CH_2{}^{\circ} \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, hexane, or
7. $CH_3{\cdot}(CH_2)_n{}^{\circ} + Na \rightarrow CH_3{\cdot}(CH_2)_n{\cdot}Na$, sodium alkyl, and
8. $CH_3{\cdot}(CH_2)_n{\cdot}Na + R{\cdot}I \rightarrow CH_3{\cdot}(CH_2)_n{\cdot}R$, an alkane $+ NaI$.

Variations of these eight reactions give rise to a large number of theoretically possible products, all of which are predictable if the results are interpreted in terms of a free radical or equivalent mechanism.

This preliminary discussion emphasizes the importance of *several* factors in determining the progress of a reaction. These are tabulated in Table I and must be considered *individually* and *collectively,* in postulating the course of any organic reaction.

Table I. Factors That Determine the Progress of a Reaction

I. Equilibrium, as determined by:
   A. The pressure,
   B. The temperature, and
   C. The solvent.

   These are important only because they change the ΔF, which determines the equilibrium.

II. Rate, as determined by:
   A. The pressure,
   B. The temperature,
   C. The concentration, and
   D. The mechanism, which may be in turn a function of:
      1. The absence or presence of a catalyst,
      2. The absence or presence of an inhibitor, and
      3. The formation of an unstable intermediate, a momentary addition compound, or an activated complex.

If Table I is approximately correct, it becomes apparent that the progress of any reaction is concerned with a number of factors. The less these variables deviate from ordinary experimental conditions, the more nearly one approaches an appraisal of the normal reactivity of a compound.

Another item for consideration in the teaching of organic chemistry is the correlation of this branch of the science with general chemistry. All too frequently the student is given the impression that general chemistry is one science and that organic chemistry is something quite different. This concept most frequently arises, perhaps, in the consideration of valence. The valence bonds of organic molecules are too often considered as typically non-polar, whereas those of inorganic compounds are regarded as polar. That this difference is one of degree rather than one of type is illustrated by the equations:

$Na^+\,{}^-Cl$, inorganic solid $+ H_2O$, excess $\rightarrow Na^+ + Cl^- + H_2O$, and

$Na^+\,{}^-O{\cdot}OC{\cdot}CH_3$, organic salt $+ H_2O$, excess $\rightarrow Na^+ + {}^-O{\cdot}OC{\cdot}CH_3 + H_2O$, and

$Na^+\,{}^-C{:}C{\cdot}H$, organic solid $+ H_2O \rightarrow H{\cdot}C{:}C{\cdot}H$, gas $+ Na^+ + OH^-$.

These equations emphasize the *relative* nature of the phenomena and indicate that in organic chemistry we should use the terms relatively electronegative and relatively electropositive instead of electronegative and electropositive (1, 3).

The relative positions of the electrons in a given system are a function of the system itself, as indicated in Figure I. In the system CH_4, CI_4, CBr_4, CCl_4 and CF_4, there is reason to believe that the electrons are displaced progressively away from the central carbon atom as the substituent groups become more strongly electronegative (or electron-attracting).

In Fig. 1 the problem of relative electronegativity has been considered from the *qualitative* viewpoint only. By a consideration of bond energies, however, Pauling has been able to evaluate the *relative* polarity of various types of bonds and set up an electronegativity map (cf Fig. 1, and Table I (3, a).

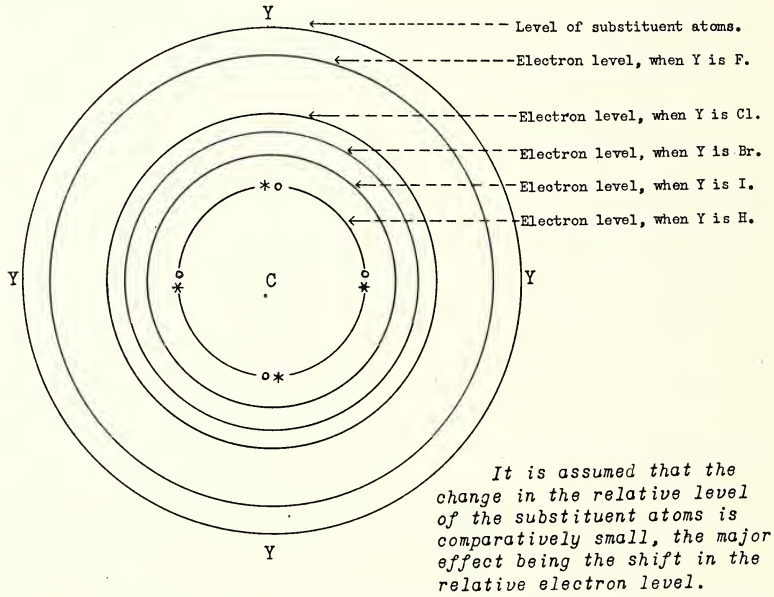

Fig. 1. Electron Level Chart. Showing the relative positions of electrons in CH_4, CI_4, CBr_4, CCl_4, and CF_4, where Y represents a hydrogen, iodine, bromine, chlorine, or fluorine atom. It is recognized that the bond distance varies with the nature of the substituent atom. The C-Br bond has a value of about 1.95 Å, and the C-Cl bond has a value of 1.81 Å, whereas the distance of the C-I bond is a little larger and that of the C-H and C-F bonds are somewhat less. Nevertheless, the general concept pictured in Figure 1 is believed to be valid.

The electronegativity map presents a graphic representation of the relative electronegativity of the various atoms with respect to the carbon atom which lies at 2.5. The atoms which lie to the right of 2.5 tend to displace the electrons away from the carbon to which they are attached, whereas those to the left of 2.5 tend to displace the electrons toward the carbon atom to which they are bonded.

This concept of the relative electronegativity of the constituent atoms of an organic molecule enables one to set up certain postulates (Table II),

which serve as a basis for predicting certain chemical properties of the compound.

Table II. Postulates of the Theory of Relative Electronegativity

1. The relative distribution of the electrons in methane is assumed to represent the condition of maximum stability for a carbon-hydrogen or hydrocarbon system, the other extreme case of stability being represented by carbon dioxide, carbon tetrafluoride, and other highly oxidized compounds.
2. Replacement of a hydrogen atom in a hydrocarbon or its derivative by a more or less strongly electronegative group is attended by a consequent distortion of the *relative* positions of the electrons.
3. Any distortion of the electron distribution from that of methane will result in a reduction in the stability of the compound so formed, and the instability will be proportional to the distortion until complete displacement of the electrons (or oxidation) is obtained.
4. Any distortion in the relative distribution of the electrons tends to be distributed throughout the system, the effect diminishing with remoteness from the point of disturbance.
5. The influence of any atom on the relative distribution of the electrons is assumed to be a function of the *relative* electronegativity of the atom concerned as indicated by the Electronegativity Map. On this basis a hydrogen atom is assigned a value of +1, an iodine or sulfur[1] atom a value of 0, a bromine atom a value of —0.75, a chlorine atom a value of —1.25, a nitrogen atom a value of —1.25, a single bonded oxygen atom a value of —2.5, and a double bonded oxygen atom a value of *something less* than —5.

By use of the postulates of Table II, it becomes possible to predict *qualitatively* the so-called addition reactions of organic compounds as indicated in Table III.

Table III. Prediction of Addition Reactions in Terms of Relative Electronegativity

1. The principal course of an olefin addition reaction, of which over two hundred fifty cases have been tabulated from the literature, is predictable by this rule with an accuracy of over 95%.
2. Every case of so-called 1,4-addition considered in terms of these postulates follows the course predictable by this rule.
3. The cases of vinylogy thus far considered are in keeping with the predictions of these postulates.
4. The addition reactions of the carbonyl group of the aldehydes and ketones are in agreement with this theory.

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[1] More recent data indicate that the sulfur atom is slightly positive with respect to the carbon atom.

5. The addition products of the nitriles, isonitriles, and similar unsaturated systems are predictable by use of these concepts.
6. Complex addition reactions such as that between (a) isobutylene and isobutane, (b) vinyl chloride and itself, (c) vinyl acetate and itself, (d) methyl methacrylate and itself, (e) isoprene and itself, and others too numerous to mention, may be predicted *qualitatively* by use of this general rule of relative electronegativity and its attendant postulates.

Consider, for example, the addition reaction of propylene with hydrogen fluoride, water, hydrogen chloride, hydrogen bromide, hydrogen iodide, chlorine fluoride, bromine fluoride, iodine fluoride, bromine chloride, iodine bromide, and hypochlorous acid. Qualitatively, the results are somewhat similar; but when quantitative data are considered it might be expected that the results would be a function of the *relative* electronegativities of the atoms concerned. Unfortunately, data are not available for this complete series, but the results that have been tabulated are in agreement with the predictions, as indicated in Table IV.

Table IV. Data That Require the Existence of Competing Reactions

$CH_3 \cdot HC\overset{+}{-}CH_2$ + $HO \cdot H$	$\rightleftarrows$ $CH_3 \cdot CHOH \cdot CH_3$, 9 to 10 parts to	
	$\rightleftarrows$ $CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$, 1 to 0 part, and	
$CH_3 \cdot HC\overset{+}{-}CH_2$ + $Cl \cdot H$[1]	$\rightleftarrows$ $CH_3 \cdot CHCl \cdot CH_3$, 5 to 6 parts to	
	$\rightleftarrows$ $CH_3 \cdot CH_2 \cdot CH_2 \cdot Cl$, 1 to 0 part, and	
$CH_3 \cdot HC\overset{+}{-}CH_2$ + $Cl \cdot I$[6]	$\rightleftarrows$ $CH_3 \cdot CHCl \cdot CH_2 \cdot I$, 3 parts to	
	$\rightleftarrows$ $CH_3 \cdot CHI \cdot CH_2 \cdot Cl$, 1 part, and	
$CH_3 \cdot HC\overset{+}{-}CH_2$ + $Cl \cdot Br$[6]	$\rightleftarrows$ $CH_3 \cdot CHCl \cdot CH_2 \cdot Br$, 7 parts to	
	$\rightleftarrows$ $CH_3 \cdot CHBr \cdot CH_2 \cdot Cl$, 5 parts, and	
$CH_3 \cdot HC\overset{+}{-}CH \cdot Br$ + HI[5]	$\rightleftarrows$ $CH_3 \cdot CHI \cdot CH_2Br$, 2 parts to	
	$\rightleftarrows$ $CH_3 \cdot CH_2 \cdot CHIBr$, 1 part.	

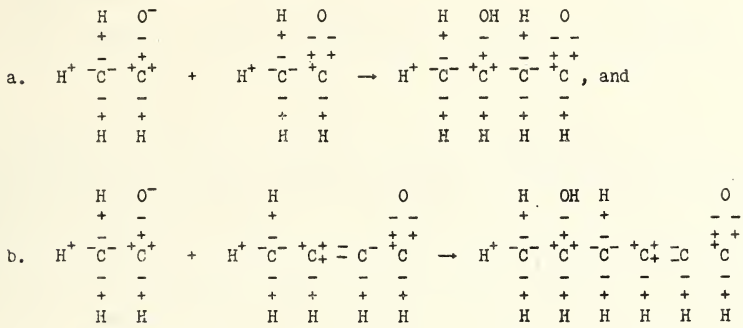
To explain the results of Table IV it seems necessary to assume an equilibrium, such as the following, in which there are competing reactions:

$$CH_3 \cdot HC\overset{+}{-}CH_2 \longrightarrow \begin{cases} + \; Cl^{-}\;{}^{+}I \rightleftarrows CH_3 \cdot CHCl \cdot CH_2 \cdot I, \text{ or} & (1) \\ \qquad \Downarrow\Uparrow \\ + \; Cl^{+}\;{}^{-}I \rightleftarrows CH_3 \cdot CHI \cdot CH_2 \cdot Cl, \text{ and} & (2) \end{cases}$$

$$CH_3 \cdot HC\overset{+}{-}CH_2 \longrightarrow \begin{cases} + \; Cl^{-}\;{}^{+}I \rightleftarrows CH_3 \cdot CHI \cdot CH_2 \cdot Cl, \text{ or} & (3) \\ \qquad \Downarrow\Uparrow \\ + \; Cl^{+}\;{}^{-}I \rightleftarrows CH_3 \cdot CHCl \cdot CH_2 \cdot I & (4) \end{cases}$$

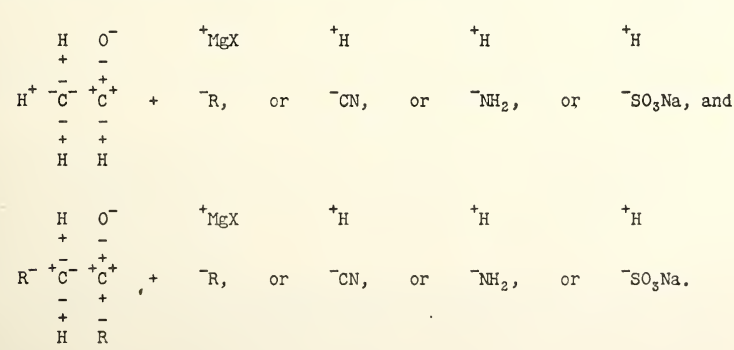
Reactions 1 and 3, presumably, account for most of the products, but as the two atoms adding at the double bond approach each other in *relative* electronegativity there is a corresponding increase in the importance of reactions 2 and 4.

The application of the principle of relative electronegativity to aldol condensation and vinylogy is illustrated by the condensation of acetaldehyde (a) with itself to give aldol, and (b) with crotonaldehyde to give 5-hydroxy-2-hexenal. In each case it is observed that a positive hydrogen atom becomes bonded to a negative oxygen atom, and that a *relatively negative carbon atom* becomes bonded to a *relatively positive carbon atom,* as:

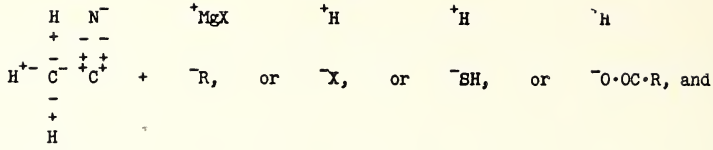


These equations suggest that an H-atom that is bonded to a strongly negative C-atom is the one that is involved in the condensation. There are in the latter case, furthermore, three *gamma* H-atoms to only one *alpha* H-atom.

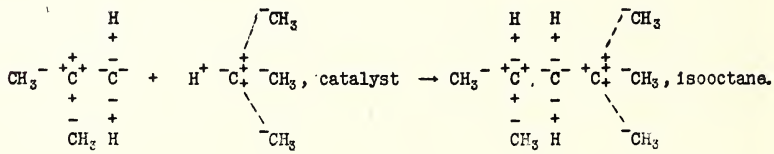
The addition reactions of the carbonyl group of the aldehydes and ketones occur in such a way that the electropositive atom becomes bonded to the oxygen atom whereas the electronegative atom becomes bonded to the carbon atom as illustrated by:



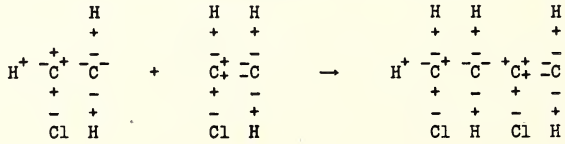
In addition reactions of the nitriles and the isonitriles, similarly, the electropositive atom adds to the nitrogen atom whereas the electronegative atom becomes bonded to the carbon atom, as indicated by:



In the reaction-types considered in the preceding paragraphs, it should be noted that all of those involving a carbon to carbon condensation take place so that a relatively positive carbon atom becomes bonded to a relatively negative carbon atom. In each of these cases, the other part of the *addend* became bonded to an atom of the opposite relative polarity. A slightly different case is now considered, in which the *ever-agreeable* hydrogen atom takes the only available position after the relative polarities of the carbon atoms have been satisfied. In the addition of isobutane to isobutylene, a *relatively* electropositive carbon atom becomes bonded to a *relatively* electronegative carbon atom, with the tertiary hydrogen atom in isobutane migrating to the *open* position in the addition complex, as indicated by:



Similarly, vinyl chloride polymerizes in accordance with the equation:



The initial polymerization product adds in turn other units of vinyl chloride, and still others to give a thread-like molecule.

Other *possible* applications of the empirical rule are (1) reactions of the ketenes, (2) ketol-enol isomerism, (3) reactions of butadiene, (4) γ-lactones and δ-lactols, (5) the Knoop *beta*-oxidation theory, (6) ionization of acids, (7) aldol condensation, (8) halogenation, (9) nitration, (10) sulfonation, (11) molecular rearrangement, (12) comparative stability, and (13) orientation. Only the compilation and correlation of

the available data in the literature, together with careful checking of questionable results, will reveal the validity and usefulness of the rule with respect to these several items.

In conclusion, it may be said that:

1. The value of this empirical rule is a direct function of its usefulness.
2. The postulate set forth herewith is given only *as an empirical rule* without any attempt to justify the applicability of the rule by a physical basis.
3. The application of this rule requires the use of the concept of alternate polarity, but without making any claims relative to the validity of the alternate polarity concept, which is generally conceded for conjugated systems but not for saturated systems.
4. The use of the rule necessitates the visualization of the organic molecule as a composite of atoms, with a number of electrical forces, as a consequence of the contribution made by each substituent atom on the chain or nucleus.
5. The rule has been applied qualitatively to over two hundred fifty cases of simple olefin addition with an accuracy of over 95 per cent.
6. Some cases of olefin addition have been considered quantitatively with a very satisfactory agreement between predictable and obtainable results (2).
7. The limitations of the application of this rule (a) to olefin addition, (b) to 1,4-addition, (c) to substitution in both the aliphatic and aromatic series, (d) to molecular rearrangements, (e) to nitrile addition, (f) to cases of vinylogy, (g) to the formation of lactones and lactols, and (h) to *beta*-oxidation, must await amplification until a complete tabulation, correlation, and interpretation of the available data have been made. The completion of these tabulations and the correlation and interpretation of the available data may lead to slight changes in the method of assigning the electronegativity values and of calculating the relative electronegativity (or R.E.) ratio.

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