

Relative Electronegativity. II. The Origin and Development of the Concept

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The current interest in relative electronegativity and the application of this concept to organic chemistry, suggests the desirability of a brief consideration of the origin, growth, and attempted applications of the idea to the reactions of organic compounds.

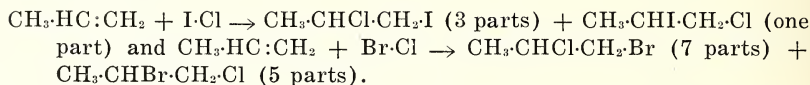
"When Benjamin Franklin encountered an electric shock by flying his kite in the summer of 1752 during a thunder storm, there was on the distant horizon a faint beam of understanding which portended the significance of this mysterious force. From that day to the present the beam has gradually but consistently broadened, yet scientists are appalled at their meagre understanding of the influence and effect of electricity on the composition and properties of matter. It is logically argued that matter is held together by electrical forces, but the exact behavior of those forces and their manifestations in the properties of compounds remain veiled with the black of mystery" (6).

The manifestations of this electrical force were observed in organic reactions by Markovnikov seventy years ago, as a result of which he formulated a rule which has come to bear his name. An English translation of his statement reads: "When an unsymmetrically constituted hydrocarbon combines with a halogen acid, the halogen of the acid adds to the less hydrogenated carbon atom, that is, to the carbon atom which is under the influence of the other carbon atoms" (28). Subsequently, he broadened his rule by stating that in the addition of a halogen acid to "vinyl chloride, chloropropylene, and other analogs," the halogen of the acid becomes bonded to the carbon atom that already supports a halogen atom.

This rule was extended by Wagner and Saytzeff (42) to cover olefins of the general type: $R\text{-HC:CH-R}'$, in which R' is the lighter of the two radicals. In such cases, they stated, the halogen of the acid becomes attached to the carbon atom that is bonded to the lighter of the alkyl substituents. The work on styrene, however, by Schramm and others casts some doubt on this rule (16, 24, 34, 38, 39).

About fifteen years later (1899) Michael generalized upon the reactions in chemistry by stating that: "Every system tends towards that state whereby the maximum chemical neutralization is reached" (30). Applied to addition reactions of the olefins, the electronegative atom or group of the addenda becomes attached to the more electropositive atom of the unsaturated molecule (29). In confirmation of this postulate, Michael carried out experiments to show that as the adding groups approach each other in relative electronegativity, increasing amounts of the reverse addition product are formed. He studied, for example, the addition

of iodine chloride and of iodine bromide to propylene and reported the following (30):



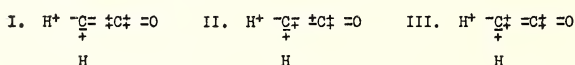
Flurschein, in 1902, stated that "the introduction of a substituent may give rise to an effect which alternates through the whole chain of the atoms" (9). This seems to have been the beginning of the latent alternate polarity concept, which was later championed by such men as Biach (1), Cuy (5), and Lapworth (25).

Ipatieff and Ogonowski (20), in 1903, from a study of the addition reactions of the olefins, postulated that the nature of the solvent and the temperature of the reaction, as well as the substituent groups, are factors in the directive addition to olefin bonds. His conclusions, since substantiated in part, suggest that there are factors which tend to intensify or mask the relative electronegativity of the particular groups concerned in the reaction.

A theoretical consideration of the polarity question from a physico-chemical viewpoint, led Biach (1) in 1905 to cite fifty-four homologous series of organic compounds which may be characterized as showing a sawtooth effect for a number of their physical constants. This line of reasoning was later championed by Cuy (5), Ceder (4), and Biltz and Balz (2).

During the next few years, Nelson, Beans, and Falk (31), and Stieglitz and Leech (37), ventured to employ the use of electronic formulas for the representation of various organic compounds and the interpretation of their reactions. Fry (10), in 1914, made use of the alternate polarity concept in writing his formula for benzene.

Four years later, Hanke and Koessler (14), reported studies on the reactions of ketene, which they cite as evidence for alternate polarity in this particular compound. They postulate three possible electronic structures for ketene, as:

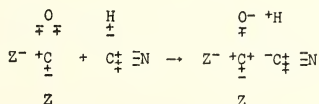


They reason that formula I, on the addition of water, should yield acetic acid as the sole product, whereas formula II should yield both acetic acid and glycollic aldehyde, and formula III should yield glycollic aldehyde as the one and only product. In view of the fact that acetic acid is the only product obtained by the addition of water to ketene, they contend that formula I is the correct representation of the electronic structure of ketene and that the compound does possess alternate polarity. This was the most conclusive evidence, of a strictly chemical nature up to this time (1918), in support of the alternate polarity concept. It is confirmed, furthermore, by the fact that the only product obtained by the addition of water to carbon suboxide is malonic acid, which clearly indicates that the relative polarity of carbon suboxide must be represented as $\text{O}^- : \text{C}^+ : \text{C}^- : \text{C}^+ : \text{O}^-$.

In the following year, 1919, Harkins and King (15) drew attention to the fact that the relative polarity of ketene is much less than that of typical organic salts.

In 1920, the physico-chemical viewpoint for alternate polarity proposed by Biach in 1905, was championed by Cuy (5). He predicted that "in a chain of carbon atoms the tendency is for these atoms to appear alternately positive and negative whenever possible". If this be true, he reasoned, each homologous series is in reality made up of two such series,—the one containing an even number of carbon atoms and the other containing an odd number of carbon atoms in the chain. As proof for his postulates of alternate polarity and dual-homologous series, Cuy cited the saw-tooth rule as applied to melting points, heats of crystallization, heats of combustion, and molecular volumes of the aliphatic acids and other series. Verkade, Hartman, and Coops (41), Carothers (3), Garner and Randall (11), Garner and Ryder (12), Smyth (35), and Kharasch (21), and others (44), have shown, however, that the saw-tooth rule does not hold for the boiling points, the refractive indices, and other properties of these same series, and consign the alternate polarity concept to the realm of the highly improbable.

Reasoning from numerous observations on addition of positive and negative groups to alternate atoms in a chain, Lapworth proposed in 1920 his theory of "alternate latent polarities" (25). According to this hypothesization, "the neighboring atoms are alternately negatively and positively polarized and this polarization is determined by what is termed key atoms" (25). The principal negative key atoms are oxygen, nitrogen, and halogens, whereas the hydrogen atoms act as slightly positive key atoms. These key atoms, by virtue of their relative electronegativity, induce alternate polarity along the carbon chain. The addition reactions of the carbonyl group, accordingly, lead to representation as ${}^{\delta-}\text{C}=\text{O}$, but this refers to the behavior of the group at the instant of reaction, and permanent polarization is not necessarily postulated. In cyanohydrin formation, the mechanism is assumed to be (25):

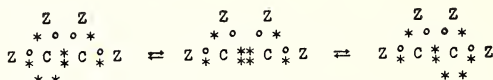


The process is reversible and the equilibrium constants for a number of cyanohydrins have been determined (25). If key atoms at the ends of a chain contribute to the same distribution, they are spoken of as acting homogeneously; otherwise as heterogeneously.

At the time when many theories of the structure of matter were being developed, the physicists arrived at a theory expressing the valence forces in terms of electrons. In particular, G. N. Lewis (26), 1923, showed that the nonionized links, with which the organic chemists are mainly concerned, could be ascribed to the sharing of valence electrons, two to each link, between the atoms. This theory was in itself somewhat in advance of the time, for the concept of shared electrons

has been hard to grasp, and we are now, over twenty years later, only beginning to realize its full meaning. By applying the Lewis concept to the Bohr structure of the atom, both theories are found to give satisfactory results.

In the following year, 1924, Carothers (3) extended the Lewis postulate for the structure of the olefin bond to include two polar and one non-polar forms, as indicated by:



in which the Z designation of one of the authors is intended to represent either a hydrogen atom or an alkyl group.

Lucas and Jameson (27), in 1924, cited evidence to show that the addition of hydrogen halides to propylene, to acrylic acid, and to dimethyl allene, as well as the rearrangement of 1-bromobutane to 2-bromobutane, can be explained as satisfactorily if not better by use of the electron displacement or "inductive effect" as by the alternate polarity concept.

In the following year (1925) Ingold and collaborators (18) began a series of articles dealing with the alternate polarity concept in the aromatic series. Their work was based on the Flursheim (9) hypothesis that the introduction of a substituent may give rise to an effect which alternates through a whole chain of atoms. It was contended that there was either an alteration in the strength of the chemical affinity or in the electric charge, real or latent, on the atoms. The alternate effect induced by key atoms was reported on by Olivier and Berger (32) in 1926 and by van Duin (40) in 1927.

In 1927 Stewart (36) stated: "The greatest problem before organic chemists at the present day is the application of modern electronic views to the salient phenomena among the reactions of organic compounds. The peculiarities of benzene, the extraordinary variety of effects observed in the rupture of double bonds, and especially the influence of conjugation, are examples of fields which seem to offer outlets for a considerable amount of speculation in connection with the G. N. Lewis theory."

Ceder (4), in 1927, and Biltz and Balz (2) in 1928, revived and supplemented the arguments of Biach (1) and Cuy (5) for the alternate polarity concept.

The idea of relative electronegativity was used by Stieglitz in his instructional work. He employed "the direction of the addition of a halogen acid as the criterion for the determination of the relative electronegativity of the two carbon atoms joined by a double bond" (43). The work was extended by Kharasch in the development of his series of relative electronegatives of some organic radicals, and this series, together with a survey of the field of relative electronegativity, was published by Kharasch and Reinmuth in 1931 (22). Subsequently Kharasch explained the peroxide effect in the directive addition of

hydrogen bromide to an olefin bond as a consequence of the formation of atomic bromine (23).

In the same year, 1931, Ingold and Smith (19, 17) began a series of articles dealing with directive addition to the olefin bond in which they investigated quantitatively the addition of hydrogen halides, iodine chloride, hypochlorous acid, and other reagents. Their work with iodine chloride on propylene checks rather closely with that of Michael some thirty-two years earlier.

In 1932, Robinson (33) published an *Outline of Electrochemical (Electronic) Theory of the Course of Organic Reactions*, which was soon followed by the appearance of the Electronegativity Map (7) of Linus Pauling.

The appearance of this map suggested to one of us a new approach to the assignment of relative electronegativity values, and the following empirical rule was formulated (8).

By regarding the organic molecule 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 a reaction.

At the present, as might be expected, the literature on relative electronegativity is confused by contradictory data, but it is hoped that time and painstaking research will bring system out of chaos and that with it will emerge a workable concept of relative electronegativity as applied to organic reactions. A good deal of progress has been made and further advances will be forthcoming, especially in the quantitative aspects of the subject (13).

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