A Correlation between the Electronegativity[1] Series of Organic Radicals and Bond Moments

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No method, free from serious theoretical objections, has yet been advanced for the determination of the relative electronegativities of organic radicals.[3] This, together with the lack of physical support for the concept of varying electron affinities of organic radicals, have been the outstanding weaknesses of the theory which have delayed its widespread acceptance. In view of the chemical evidence which proponents of the theory have advanced,[4] one cannot doubt that the electronegativity series actually represents a definite *chemical* reality. But still unsettled is the question whether the electronic picture, by means of which the electronegativity theory has been illustrated, represents a *physical* reality.

The application of the principles of electric moments offers the greatest promise of removing these difficulties. The magnitude of the electric moment of a covalent bond is a measure of the electronic dissymmetry of that bond. If a number of radicals, R′, R″, R‴, can be arranged in a series of decreasing affinity for electrons, it should follow that if these radicals are combined with a suitable reference radical X, the electric moment due to the bond R–X should decrease in the order R‴ – X, R″ – X, R′ – X (Fig. 1).

Electro   R′ :   R′ :X   Electric
    negativity   R″ :   R″ :X   moment
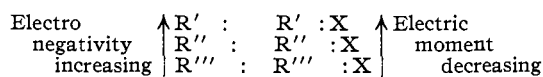   increasing   R‴ :   R‴ :X   decreasing

Fig. 1.—Theoretical relationship between electric moment and electronegativity.

The choice of the reference radical is limited to the halogens for the following reasons. First, the reference radical must be strongly electronegative in character in order that the value of the bond moment R–X be considerably larger than the usual experimental errors of measurement. Second, the radical should have a stable electronic structure of small polarizability, so that

the variation of the bond moment may be a reasonably accurate measure of the variation in the electronegativity of the organic radical. Third, the reference radical must be monoatomic; otherwise difficulties would arise in disentangling variations in the value of the R–X bond moment from the variations in the moments of the individual bonds in the polyatomic reference radical. Finally, the reference radical must be monovalent in order to avoid the uncertainties which otherwise would arise from our meager knowledge of bond angles and of the mutual effect of neighboring dipoles.

On the basis of these considerations, the fluorine atom is the most promising reference radical. It is monovalent, strongly electronegative, and possesses a stable electronic structure of small polarizability. Unfortunately, the electric moments of but few fluorides have been measured; and, due to the chemical nature of secondary and tertiary alkyl fluorides,[5] it is improbable that these data can be determined with sufficient accuracy to be of use for this purpose.

Obviously, the chlorine atom is the next best choice. But due to the fact that the polarizability of this atom is comparatively large, the values of the R–Cl bond moments will not measure the absolute electronegativity of the organic radicals. However, since the polarization of the chlorine atom may be expected to be a function of the electronegativity of the organic radical to which it is combined, the relative magnitudes of the bond moments should not be changed.[6]

In Table I are listed some representative organic chlorides in the order of increasing values of the electric moment due to the carbon–chlorine bond. In those cases in which the electric moment of the molecule is the vector sum of two moments, the contribution of the second moment

(1) The electronegativity of an organic radical has been interpreted as the "affinity of that radical for the pair of valence electrons." Kharasch and Marker, THIS JOURNAL, **48**, 3131 (1926).

(2) Eli Lilly Fellow, 1938–1939.

(3) Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, 1929, pp. 26–39. This reference contains an excellent summary of a number of methods which have been utilized for this purpose.

(4) Kharasch, Reinmuth, *et al. J. Chem. Ed.*, **6**, 404–418 (1929); **8**, 1703–1748 (1931); **11**, 82–96 (1934); **13**, 7–19 (1936).
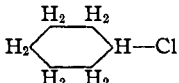
(5) Henne and Midgley, THIS JOURNAL, **58**, 882–884 (1936).

(6) In other words, the variations in the values of these bond moments cannot be used for predicting quantitatively the differences in the degree of electronegativity. For example, if the R–Cl bond moments of three organic chlorides, R′–Cl, R″–Cl, R‴–Cl, have values of 1.0, 1.4, and 2.0 *D*, respectively, we would be justified in predicting that the relative electronegativity of the three radicals varies in the same order; but we could not state that of the three radicals, R″ must be closer to R′, rather than R‴, in degree of electronegativity.

TABLE I

ORGANIC CHLORIDES ARRANGED IN THE ORDER OF INCREASING CARBON–CHLORINE BOND MOMENTS

Where the electric moment has been measured in the gas phase, this value has been taken as the correct value. The values measured by the solvent method have been corrected for the solvent effect (Note 9) and this corrected value listed as μ Average. Values which are probably correct to 0.01 to 0.02 Debye units have been given to two places. In cases where there is some doubt as to the correct value of the electric moment, or where uncertainties have been intro- duced by the assumptions made in eliminating the contributions of other dipoles in the molecule, the values of the electric moment have been given only to 0.1 Debye unit.

Name of radical R	Formula of RCl	μ RH		μ R–Cl (solvent)		μ R–Cl (gas)		μ Average
Phenylethynyl	$C_6H_5C\equiv C-Cl$	0.6[a]		1.10[b]				0.5
Phenylvinyl	$C_6H_5CH=CH-Cl$	0.3[c]		1.40[d]				1.2
Methylvinyl	$CH_3CH=CH-Cl$	0.35[e]				1.66[f]		1.4
Vinyl	$H_2=CH-Cl$	0				1.66[g]		1.66
Tolyl	$CH_3C_6H_4-Cl$	0.37[e]		1.94	1.95[h]			1.68
Phenyl	C_6H_5-Cl	0				1.70	1.73[i]	1.71
Methyl	CH_3-Cl	0	1.87			1.88	1.86[j]	1.87
Ethyl	C_2H_5-Cl	0	2.06			2.06	2.04[j]	2.05
n-Propyl	$CH_3(CH_2)_2-Cl$	0				2.10[j]		2.10
n-Butyl	$CH_3(CH_2)_3-Cl$	0				2.11[j]		2.11
n-Amyl	$CH_3(CH_2)_4-Cl$	0				2.12[j]		2.11
Isopropyl	$(CH_3)_2CH-Cl$	0				2.15[j]		2.15
Cyclohexyl	$H_2C(CH_2)_4(H_2)CH-Cl$	0		2.07	2.10[k]			2.22
Allyl	$CH_2=CHCH_2-Cl$	0.35[e]				1.99	2.01[l]	2.2
Benzyl	$C_6H_5CH_2-Cl$	0.37[e]		1.87	1.85[m]			2.2
t-Butyl	$(CH_3)_3C-Cl$	0		2.15	2.14[n]			2.29
Benzhydryl	$(C_6H_5)_2CH-Cl$	0.4[o]		1.9[p]				2.3
Triphenylmethyl	$(C_6H_5)_3C-Cl$	0.6[q]		1.9[r]				2.6

[a] Otto and Wenzke, THIS JOURNAL, **56**, 1315 (1934).   [b] Wilson and Wenzke, *ibid.*, **56**, 2027 (1934).   [c] Otto and Wenzke, *ibid.*, **57**, 295 (1935).   [d] Bergmann, *J. Chem. Soc.*, 404 (1936).   [e] McAlpine and Smyth, THIS JOURNAL, **55**, 459 (1933). [f] Hojendahl, "Studies of Dipole Moment," Copenhagen, 1928.   [g] Sugden, *Trans. Faraday Soc.*, **30**, 796 (1934). The experimental data from which this value is calculated could not be found. However, the relative values for vinyl bromide, 1.48[f], and phenyl bromide, 1.6 (gas value calculated from solvent data), also place the vinyl radical in this position, above the phenyl radical.   [h] Tiganik, *Z. physik. Chem.*, **B13**, 447 (1931); Wolf and Trieschmann, *ibid.*, **B14**, 347 (1931).   [i] McAlpine and Smyth, *J. Chem. Phys.*, **3**, 56 (1935); Groves and Sugden, *J. Chem. Soc.*, 972 (1935).   [j] Calculated by Groves and Sugden, *ibid.*, 158–162 (1937), assuming $P_A = 5\%$.   [k] Hassel and Naeshagen, *Z. physik. Chem.*, **B15**, 375 (1932); **B19**, 442 (1932).   [l] Gupta, *Nature*, **125**, 600 (1930); Mahanti, *Physik. Z.*, **31**, 548 (1930).   [m] Weissberger and R. Sängewald, *Z. physik. Chem.*, **B9**, 139 (1930); Parts, *ibid.*, **B12**, 324 (1931).   [n] Parts, *ibid.*, **B7**, 336 (1930); Smyth and Dornte, THIS JOURNAL, **53**, 551 (1931).   [o] Estermann, *Z. physik. Chem.*, **B1**, 144 (1928); Riedinger, *Physik. Z.*, **39**, 380 (1938).   [p] Weissberger and Sängewald, *Z. physik. Chem.*, **B20**, 150 (1933).   [q] Bergmann, Engel and Wolf, *ibid.*, **B17**, 85 (1932).   [r] Bergmann, Engel and Wolf, *ibid.*, **B17**, 85 (1932); Smyth and Dornte, THIS JOURNAL, **53**, 551 (1931).

has been calculated and eliminated. A few ex- amples will clarify the procedure which has been followed. Phenyl, methyl, and ethyl chlorides
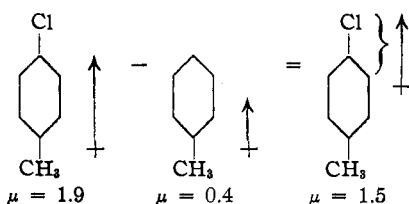

Fig. 2.—Calculation of the tolyl-chlorine bond moment.

have electric moments[7] of 1.71, 1.87, 2.05, re- spectively. Since there are no other dipoles in

(7) All moments in this paper are expressed in Debye units.

the molecule, we can say that the variation in the value of the moment is due to the variation in the electronegativity of the phenyl, methyl, and ethyl radicals.[8] To obtain the value of the tolyl- chlorine bond moment, the value 0.4 (for toluene) is subtracted from the electric moment of p- chlorotoluene, 1.9. The result, 1.5, places the tolyl radical above the phenyl radical in this series (Fig. 2).

(8) It has been pointed out frequently that the value of the elec- tric moment of a molecule such as methyl chloride is the vector sum of the carbon–chlorine and the carbon–hydrogen bond moments. This fact does not alter the above argument. The value of the carbon–hydrogen bond moment is very small, and in any case would be expected to vary with the electronegativity of the radical. Thus it follows that the relative values of the R–Cl bond moments will not be changed.

In such cases where the moments in the molecule are directed at an angle, e. g., benzyl chloride and allyl chloride, the correction is complicated by two factors: the uncertainties arising from our lack of knowledge concerning the size of the bond angles in these molecules and the effects of neighboring dipoles upon each other. These difficulties have necessitated introducing approximations in such cases. The bond angle has been taken as 110°, and the phenyl–carbon ($C_6H_5 \longleftarrow + C_{aliph.}$) and vinyl–carbon ($H_2C{=}CH \longleftarrow + C_{aliph.}$) bond moments have been assumed to have the same value in these compounds that they possess in toluene and propylene.

A further complication arises in attempting to utilize the data available in the literature. The value of the electric moment varies according to the method used for its measurement—in solution or as a vapor. In order to make the two groups of data comparable, the solution values have been corrected for the "solvent effect" by the use of Müller's equation.[9]

In view of these difficulties, it is remarkable to find that the series of radicals set up in this manner agrees so well with the electronegativity series, based upon the selective hydrolytic splitting of unsymmetrical organo-mercurials.[10]

TABLE II

ELECTRONEGATIVITY SERIES OF ORGANIC RADICALS

Anisyl > naphthyl > tolyl > phenyl > methyl > ethyl > n-propyl > isopropyl > cyclohexyl > benzyl > t-butyl > diphenylmethyl[a] > triphenylmethyl[a]

[a] Not determined from hydrolytic splitting of the mercuric compounds.

As mentioned previously, no theoretically sound chemical method for the determination of the relative electronegativity of organic radicals is available. The procedure advocated by Kharasch has yielded consistent results, and appears to be the best of the many which have been proposed. However, objections to this method have been raised because of its dependence upon competing reaction rates.[11]

At first thought it might appear that the correlation which exists between the data of electric moments and electronegativity would solve the problem. Unfortunately, this is not the case. While it is true that this correlation should prove useful in establishing the relative electronegativity of certain types of organic radicals, in applying the method there arise a number of difficulties (some of which have been encountered previously) which necessarily lead to the belief that the chemical method must continue to be the organic chemists' main reliance in measuring electronegativity.

Among these difficulties are the following:
1. The experimental accuracy of dipole moment measurement is still unsatisfactory. For example, the electric moment of p-chlorobiphenyl has been reported by the same workers at four different times[12] as 1.49, 1.30, 1.53 and 1.63. Obviously, on the basis of these results, it is impossible to assign the biphenyl radical a definite position in the electronegativity series (Table I).

2. The electric moment procedure is far less sensitive than the chemical method. For example, the Kharasch method easily distinguishes between the electronegativity of the o-, m- and p-tolyl radicals; electric moment data cannot. Further, the dipole data of the n-propyl, n-butyl and n-amyl chlorides can only tentatively place these radicals in the order shown (Table I)—the differences in the values of the moments are of the same order of magnitude as the experimental error (0.01 D in these cases). On the other hand, the results of the chemical method definitely assign these radicals their consecutive positions.

3. Our knowledge of bond angles is meager. The vast majority of organic radicals possess more than one moment in the chloro derivative. In order to determine accurately the value of the bond moment, a correction must be made for the contribution of these other moments in the molecule; this requires knowledge of the angles at which these dipoles are directed. The value of these angles is uncertain.

4. We cannot correct for the polarization effects when the radical R contains a group of high polarizability. That is, the contribution of an easily polarizable group in the radical R will not have the same value in the molecule RH that it has in the molecule RCl.

It is for these last two reasons that the data in Table I are restricted to the more common hydrocarbon radicals which possess a fair degree of symmetry. In spite of these difficulties, electric moment data still can be of value in establishing

(9) Müller, Trans. Faraday Soc., 30, 729 (1934).

(10) Kharasch, et al., THIS JOURNAL, 48, 3130–3143 (1926); 54, 674–692 (1932).

(11) Adkins, J. Chem. Ed., 9, 1865–1873 (1932); see also the discussion by Kharasch, Reinmuth and Mayo, ibid., 11, 83–84 (1934).

(12) Weissberger and Sängewald, Z. physik. Chem., B9, 133 (1930); B13, 383 (1931); B20, 145 (1933); Hampson and Weissberger, THIS JOURNAL, 58, 2111 (1936).

the relative electronegativity of some of the more simple radicals. For example, the position of the allyl, vinyl, phenylvinyl, and phenylethynyl radicals in the electronegativity series has not been established experimentally. On the basis of the data available, it may be predicted that these radicals must be placed in the series at the positions assigned to them in Table I.

The correlation shown to exist between electronegativity and electric moment may have another application. In case the electronegativity of a simple organic radical R has been determined, the value of the electric moment of the halogen derivative RX may be predicted. Thus, it has been shown lately that the electronegativity of the neopentyl radical is of the same order of magnitude as that of the t-butyl radical.[13] On the basis of this information it may be predicted that the electric moment of neopentyl chloride will be found to be equal to that of t-butyl chloride.

That the "electron affinity" of each radical may be considered to be a constant quantity (to a first approximation), which does not vary greatly with the environment, is illustrated by the data in Fig. 3. If the phenyl radical is united with the
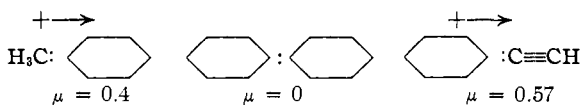

Fig. 3.

less electronegative methyl radical, the molecule possesses a moment with the negative end directed *toward* the phenyl group. On the other hand, if the very strongly electronegative ethynyl group is combined with the phenyl radical, the electric moment of the resulting molecule is directed in the opposite direction, *away* from the phenyl group.

(13) Whitmore and Bernstein, THIS JOURNAL, **60**, 2625 (1938).

In this paper the writer has correlated the variation of the carbon–chlorine bond moment with the concept of electronegativity of organic radicals. This variation has been interpreted previously by the use of such physical concepts as induction[14] and resonance.[15] On the other hand, the electronegativity series is based upon the relative rates of competing reactions. There can be little doubt that *those physical factors which operate to vary the magnitude of the carbon–chlorine bond moment affect to a similar degree the relative rates of these competing reactions, a purely chemical property.*

Summary

1. The series of organic radicals obtained by arranging the chloro derivatives of these radicals, R–Cl, in the order of increasing values of their carbon–chlorine bond moments is identical with the electronegativity series of organic radicals established by the study of the selective hydrolytic splitting of organomercurials.

2. Due to this correlation, it is possible to assign positions in the series to a number of radicals from the reported values of the electric moments of the corresponding chlorides. Among the radicals which can be placed by this means are allyl, vinyl, phenylvinyl, and phenylethynyl.

3. The *physical* factors, resonance and induction, which have been used previously to interpret the variation in magnitudes of the moments of organic chlorides, appear to be the same factors which determine the electronegativity of organic radicals as measured by *chemical* methods.

(14) Smyth, *Trans. Faraday Soc.*, **30**, 752–758 (1934).

(15) Ingold, *Chem. Rev.*, **15**, 253 (1934); Sutton, *Proc. Roy. Soc.*, **133A**, 668–695(1931); *Trans. Faraday Soc.*, **30**, 789–801(1934).