THE THEORY OF PARTIAL POLARITY OF THE ETHYLENE BOND AND THE EXISTENCE OF ELECTRO-ISOMERISM

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INTRODUCTION

Many rules have been proposed regarding the addition of unsymmetrical reagents to compounds containing double bonds. A careful search of the literature, however, reveals numerous exceptions to any of the rules thus far formulated. In the present paper the writers propose a theory for the addition reactions of compounds of the ethylene type, which in their estimation is in agreement with the facts available in the literature. In the case of 2-pentene, where the evidence seemed to point against the theory proposed, the writers have been able to demonstrate the existence of two forms of the 2-pentene which add the halogen acid in a different ratio than that recorded in the literature.

GENERAL CONSIDERATION OF PREVIOUS THEORIES

a. Electronic theories proposed

With the advent of the electronic conception of valence, a number of theories appeared which attempted to explain and amplify the reactions of unsaturated derivatives as given in the rules of Markownikow, (1) Saytzeff (2), and Ipatiew[1] and also to account for the facts observed by other investigators. Only the outstanding theories will be considered here.

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[1] Ipatiew [Ber. **36**, 1988 (1903): Chem. Zentr. **70**, II, 17 (1899)] had a broad understanding of the subject for he believed that the position taken by the halogen, when a halogen acid is added to a double bond, is determined by the nature of the radicals linked to the carbon atoms of the double bond, the nature of the solvent, and the temperature.

The two electronic theories which have gained vogue are those of Lewis (3) and Cuy (4). Two attempts have been made to extend the Lewis theory by making specific assumptions, one by Carothers and the other by Lucas and his collaborators.

b. Discussion of theory of alternating polarity

The Cuy theory of alternating polarity has attracted much attention and has, because of its weakness, even been used as an argument against the application of the electronic concept to organic compounds. A careful perusal of Cuy's articles disclosed the weaknesses of the argument that there is an alternation in the charges on carbon atoms. The whole theory was shown, in the able paper of Lucas and Jameson (5), to be built upon erroneous assumptions. The strongest argument that Cuy believes he possesses, namely the alternation in melting points of homologous series, is undoubtedly due to differences in the crystal lattice structure. Thus, Verkade, Hartman and Coops (6) show definitely that the phenomenon of oscillation of heats of combustion of dicarboxylic acids of the oxalic acid series, observed by Stohmann, Kleber, Langbein and Offenhauer (7), holds up to C_{13}, the variation amounting on the average to 3 kgm. cal. per mole. (i.e., in one series the addition of CH_2 amounts to 158 kgm. cal., while in the other series it is only 155 kgm. cal.). The oscillation, however, disappears completely when the liquid esters of the same series are considered (8). Thermally the liquid esters constitute a single homologous series. Verkade, Coops and Hartman also point out that oscillation has been observed with fatty acids in the case of the following properties:

1. Melting point
2. Heats of crystallization (9)
3. Heats of combustion of crystalline acids (10)
4. Molecular volumes of crystalline acids (11)

but no oscillation has ever been observed with

1. Boiling points
2. Molecular refraction of the liquid acids (12)
3. Heats of combustion of liquid acids (10)
4. Molecular volumes of the liquid acids (11)

Hence the even and odd terms of the homologous series may have different crystal structures.[2] This view is rather an extension of the views of Garner and Randall (9), based on their work and also that of Muller and Shearer (13) on the heats of crystallization of fatty acids. There is thus no justification for this bit of evidence adduced by Cuy. The other three lines of argument, namely, (*a*) the addition of halogen acids to ethylene derivatives, (*b*) addition of halogen acids to hydrocarbons of the allene series, (*c*) rearrangement of alkyl bromides, have been shown by Lucas and Jameson to be without any justification.

These arguments against the theory of alternate polarity are reiterated at some length here for the hypothesis has taken root (14) and considerable experimental work was even done to disprove the hypothesis. It is also quoted quite often as an hypothesis of merit. We believe, however, in view of all that has been stated before, that the facts upon which this hypothesis is built are in themselves, when critically examined, the best argument against the theory.

The second electronic theory of the double bond was presented by Lewis (3) and elaborated upon by Carothers (15) and by Lucas (5) and his collaborators. However, before discussing these theories it would be well to state our own hypothesis so that we may show in what ways we depart from the views of these authors.

HYPOTHESIS OF THE DOUBLE BOND BETWEEN CARBON ATOMS FROM THE STANDPOINT OF THE THEORY OF PARTIAL POLARITY

a. Basis of theoretical concepts

The general basis for this concept of the double bond is discussed in papers by Kharasch and Sher (16) and Kharasch and Marker (17). In this first paper an attempt was made to correlate the electronic structure of organic substances with the total

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[2] Cf. however, the paper by Pauly (Z. anorg. allgem. chem. **119**, 271 (1921) and also Garner and Randall (loc. cit.). The discussion of this paper is held in abeyance for Prof. Verkade promises to discuss it in a future publication. However, a critical review of these papers by the reader will convince him that the conclusions of Verkade, Coops and Hartman are in no way invalidated.

amount of heat they furnish upon combustion. The reference positions, to which the positions occupied by the electrons in all types of organic molecules are compared, are those occupied by the eight valence electrons around the carbon nuclei in methane and in carbon dioxide respectively. Furthermore, it is assumed that the displacement of electrons from the methane arrangement to that of carbon dioxide occurs in stages. This postulate is, of course, a corollary to the Bohr conception that around each atomic center there exists a particular set of energy levels. The postulate concerns itself only with those energy levels that lie outside the normal valence energy levels and the displacement of the electrons from the valence energy levels into outside energy levels. Hence reference to the eight electrons of methane is to their location in the normal valence energy level.[3]

The above postulate also implies that two atoms can share a pair of electrons in any of their respective energy levels and that the kinetic and potential energy of the system will depend upon the electronic structure of the molecule. To make clearer the meaning implied by this last statement, let the arcs in figure 1 represent some of the possible energy levels which electron pairs may occupy in carbon atoms *A* and *B*, respectively.

It is readily seen that two carbon atoms can hold a pair of electrons in various manners which entail varying degrees of polarity. The position of these shared electrons with respect to their individual valence orbits will depend upon the affinity of the two atoms for electrons and the nature of the other atoms attached to A and B. Thus, if the atom A, due to the nature of radicles attached to it has a greater affinity for electrons than does atom *B*, we may assume that the two electrons will be in the first

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[3] The adoption of this terminology does not commit us to any specific mechanical theory of the structure of the atom. If there existed a detailed and commonly acceptable model of the carbon atom, it would be possible to translate our theory into terms of that model. It would be still more convenient, however, for all practical purposes to employ a more schematic representation. Therefore, in directing the attention to figure 1, we particularly desire to emphasize the fact that no portrayal of actual electronic paths is attempted. The figure indicates only a sufficient number of energy levels to illustrate conveniently the concept we desire to advance.

energy level of *A* and the fourth energy level of *B* as indicated by diamonds in the figure. Other positions are also possible, for instance, the first energy level of *A* and the third energy level of *B*, as indicated by circles in the figure. The two atoms may thus share a pair of electrons in such a way as to give rise to various degrees of polarity. It is also quite possible that, if due to the nature of radicals attached to it, *A* has a slight affinity for electrons, it would tend to hold the electrons in some outer energy level, and if *B* has the same radicals attached to it, they would both tend to share the electrons in some outer energy level, as denoted by 4A and 4B in figure 1. This would undoubtedly contribute to the instability of the molecule.

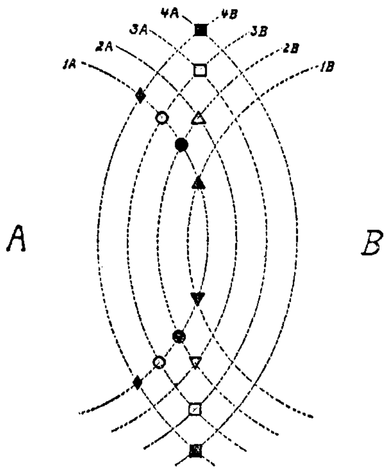

FIG. 1. SCHEMATIC REPRESENTATION OF THE BOND BETWEEN TWO CARBON ATOMS AND SOME POSSIBLE VARIATIONS THEREOF

b. Types of bonds in organic molecules and their heat value

We have thus, as far as the energy of the organic molecules are concerned, to consider that the possibilities shown in figure 2 exist in the sharing of electrons.

The lines in figure 2 represent the distances of the electrons forming the bond from the two carbon nuclei, A and B. We assume also that the pair of valence electrons held together by two carbon atoms in saturated hydrocarbon i.e. type (1) is intermediate between their respective normal energy levels and the level which the electrons occupy in carbon dioxide. The net energy which they supply upon combustion is thus the same as if we had a pair of electrons in the valence shell of one carbon atom of the methane type. This rather plausible assumption is well justified by the agreement between calculated and observed values.

Accordingly if the expression for the heat of combustion of compounds of the type (1) is given by the expression $Q = 26.05\ N$,

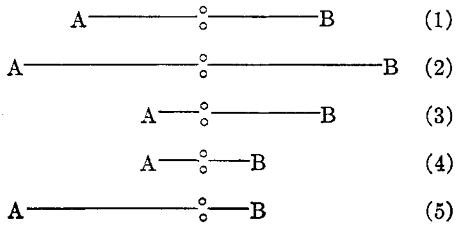

FIG. 2. TYPES OF BONDS IN ORGANIC MOLECULES

(1) Type of bond characteristic of aliphatic hydrocarbon, with ethane as a representative compound; (2) a bond in which both groups joined are weakly electronegative as in the case of the two carboxyls forming oxalic acid, or two triphenylmethyl nuclei; (3) a bond between a moderately electronegative radical (such as methyl) and a strongly electronegative radical like phenyl or naphthyl; (4) a bond between two highly electronegative radicals, such as phenyl or naphthyl; (5) a bond between a highly electronegative radical (such as phenyl or naphthyl) and a very weakly electronegative radical (such as carboxyl). Type 5 may be considered as a special case of type 3.

where N denotes the number of electrons, then if 2, 3, 4, 5 differ from (1) only in the arrangement of the one pair of electrons, the expressions for the heats of combustion of these compounds should be:

1. $Q = 26.05\ N$
2. $Q = 26.05\ N + a$
3. $Q = 26.05\ N - b$
4. $Q = 26.05\ N - c$, where c is larger than b
5. $Q = 26.05\ N + d$

In case of compounds of type (1), the agreement within experimental error of the calculated heats of combustion of some thirtyone saturated hydrocarbons with the experimentally determined values, indicates the plausibility and at least the approximate correctness of the hypothesis. This is merely a rough approximation to the truth, but until more refined experimental methods of attack are available the hypothesis covers the ground adequately.

This attack on the problem suggests immediately that in case of sharing of electrons as represented in type (2), the molecule contains a larger amount of energy, namely that necessary to pull the electrons out from the "normal" energy levels of atoms *A* and B into the outer energy levels. Upon combustion this molecule should furnish a larger amount of heat than calculated upon the assumption applicable to type (1). Unfortunately, the data at hand do not allow us to draw far-reaching conclusions. Thus, Schmidlin (18) determined the heat of combustion of a molecule which we should consider to have a bond of type (2) between the two carbon atoms, namely triphenyl methyl or hexaphenyl ethane. Our calculations, assuming the C-C bond to be similar to (1), give 2370.4 kgm. cal. for the heat of combustion, while Schmidlin obtained 2381.0 kgm. cal. The difference between the two values, namely 10.6 kgm. cal.[4] could be ascribed to the potential energy accumulated in the molecule when the valence electron was moved out from the "normal" energy level into a position corresponding to bond (2). It is noticeable, however that the difference amounts to only 0.5 per cent, which could well be within the limits of experimental error of Schmidlin's determinations. The evidence is not sufficient to be admissible as proof of the validity of our argument. The purely chemical evidence, however, is much better and is in perfect agreement with our hypothesis.

The bond corresponding to type (3) and (4) is encountered when two strongly electronegative radicals share a pair of valence electrons. Due to the great attraction of each one of those radicals for electrons, they share these electrons more in the inner shells than do those which are not so strongly electronegative. The total energy which such molecules furnish upon

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[4] This difference is really even larger because the calculated value refers to the liquid state, while Schmidlin's value is that of the solid compound.

combustion would, therefore, be smaller, for it would require more energy to displace the electrons into the outermost energy levels. The radicals which would begin to exhibit that tendency are all those that appear above the methyl radical in our table of electronegativity of radicals (17).

This is the basis of the footnote on page 639 in the paper by Kharasch and Sher:

> "It is most significant that for most benzene hydrocarbons the calculated value is somewhat higher than the experimentally determined value. This is due to a diminution of the energy of the system due to the benzene nucleus. Once this is taken into account in the calculation of the heat of combustion the agreement is then even more striking. It is omitted here in order to avoid confusion and will be discussed in detail in a later publication."

This, however, would imply a sharing of electrons in different energy levels for every different case, i.e. a formula which would express the sharing of electrons in different energy levels between a methyl and a phenyl radical would not express that for an ethyl and a phenyl radical. No doubt this notion is correct, but the increment is so slight as to be utterly imcomparable to the normal experimental error. In bonds of type (3) and (4) b and c have the following numerical value: $b = 3.5$ kgm. cal., $c = 6.5$ kgm. cal. The value for c is larger than b because a bond of type (4) corresponds to a pair of valence electrons held in common by two strongly electronegative radicals.[5]

The heat of combustion of benzene hydrocarbons of the type (3) then becomes $Q = 26.05 \times N - 3.5A$, where A corresponds to a number of other carbon atoms which are directly linked to the benzene nucleus, and which lie below the phenyl radical in the table of electronegativity of radicals. Thus, A is 1 in toluene, 2 in xylene, 3 in mesitylene, etc. The calculated values agree remarkably well with the experimentally determined values, at all times well within the limits of experimental error. Similarly,

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[5] Similar considerations would undoubtedly apply to other types of compounds, which are made up of strongly electronegative radicals: phenols, aromatic ethers, etc.

the heat of combustion of benzene hydrocarbons, corresponding to bond (4) is given by the expression $Q = 26.05 \times N - 6.5\,B$, where B corresponds to the number of bonds between two electronegative radicals. Thus B is 1 in diphenyl, and 2 in p-diphenyl phenylene.

c. Heats of combustion of compounds containing double bonds and deductions therefrom

When the heat of combustion of a substituted ethylene derivative, say hexylene, is calculated on the same basis as was used for the heat of combustion of a saturated hydrocarbon,[6] we obtain a value of $Q = 26.05 \times 36 = 937.8$ kgm. cal. per mole, while the experimentally determined value is 952.6 kgm. cal. Such a large difference between the calculated and the determined value is significant in view of the fact that the agreement for the saturated hydrocarbons was within two tenths of one per cent. Furthermore, all unsaturated derivatives of the ethylene type give more heat upon combustion than that calculated by assuming that all the electrons are shared in a manner similar to that of the saturated hydrocarbons. The difference is almost constant within the limits of experimental error and amounts to about 13 kgm. cal. per mole.

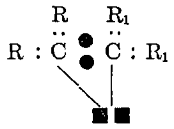

FIG. 3

Upon the basis of the view of molecular energy content developed, this difference is ascribed to the fact that the second pair of electrons held between the two carbon atoms is displaced from the normal valence energy levels of one or both of the carbon

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[6] The general formula for the heat of combustion with oxygen of a saturated hydrocarbon is given by the expression $Q = 26.05\,N$, where Q is the molecular heat of combustion and N the number of electrons in the molecule, while 26.05 is the heat liberated by the inter-displacement of an electron from the methane "normal" energy level to that of the energy level of carbon dioxide type.

atoms. Furthermore, from the chemical evidence, which we shall adduce later, we conclude that there is a definite polarity at a double bond. Our total picture of the double bond in light of these facts may be formulated as in figure 3, where the circles denote the pair of valence electrons of unsaturated compounds which are of no consequence as far as addition reactions of the double bond are concerned. They may be bonds of the type 1, 2, 3 or even 4 depending upon the nature of the radicals R and R_1. Their relative position would be of consequence only in the thermal behavior of the substance. The other pair of electrons, marked with squares, is the important one and the figure is intended to show that this pair of electrons is decidedly displaced from the carbon atom holding the R radicals so as to be in the outer energy levels of that atom, and is not so far displaced from the normal valence orbit of the carbon atom holding the radicals R_1. Of course, whether these electrons are in energy level 1, 2, 3 or 4 would depend upon the nature of the radicals R and R_1.[7]

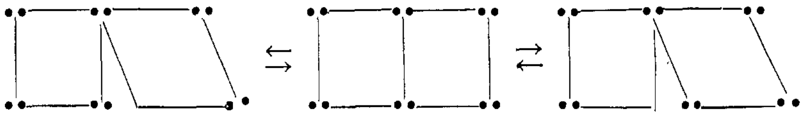

FIG. 4

This is our general picture which, for the sake of clarity, is purposely devoid of such refinements which atomic structure information would allow us to add. However, to transform this into a useful hypothesis, we must add the following postulates:

d. Postulates of theory of partial polarity

Postulate I. There is a definite polarity at the double bond, so that unsaturated derivatives of the ethylene type have a definite

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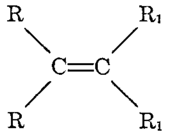
[7] It is evident from this concept that while we are employing the factor 13 kgm. cal. for the displaced electrons in ethylene compounds the latter value need not necessarily be the same for all types of unsaturated derivatives. Thus, it may be 9 kgm. cal. for some types and 16 kgm. cal. for others. The actual displacements cannot be determined within certain limits solely from consideration of heats of combustion, for the experimental errors involved are within these limits.

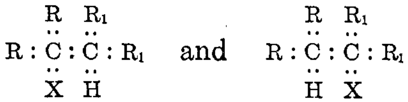
electrical polarization in at least one part of the molecule. We are rather reluctant to suppose that unsaturated derivatives, in which the radicals attached to the carbon atoms of the double bond are different, possess a structure as indicated in figure 4 and used by Carothers.

Forms II and III are assumed by Carothers to be capable of only momentary existence so that the concentration of the active forms is always small; the dissociations are assumed to be negligible so that there is equilibrium between the active forms and the inactive. We believe, and will prove later that there is no real evidence for the assumption that carbon compounds assume such an inactive form but that the directive addition reactions of unsaturated derivatives indicate that we have either Form II or III.

Postulate II. In the case where the radicals attached to the carbon atoms of the double bond are about the same in electronegativity (see Postulate VI) it is possible to produce either Form II or Form III. These two forms are electro-isomers. At no time do we assume, however, that these two forms are in equilibrium, through Form I. This postulate implies that if by the addition of a molecule of HX to an ethylene derivative

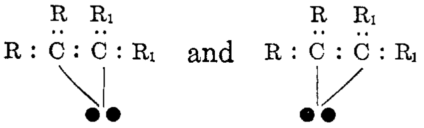


we obtain two products



$$\begin{array}{ccccccc} & & R & & R_1 & & \\ R & : & \ddot{\underset{\cdot\cdot}{C}} & : & \ddot{\underset{\cdot\cdot}{C}} & : & R_1 \\ & & X & & H & & \end{array} \quad \text{and} \quad \begin{array}{ccccccc} & & R & & R_1 & & \\ R & : & \ddot{\underset{\cdot\cdot}{C}} & : & \ddot{\underset{\cdot\cdot}{C}} & : & R_1 \\ & & H & & X & & \end{array}$$

and that they arose through the presence in the solution of two electro-isomers:



respectively. It is implied also, that one of the electro-isomers is more stable and that while it is possible to transform one electro-isomer into another, the two are not in equilibrium[8] for the transformation of one into the other would be accompanied by a change in the energy of the system.

Postulate III. The second pair of electrons constituting the double bond is always held in outer energy levels of one of the carbon atoms and some closer inner energy levels of the other, the particular energy level depending upon the nature of the radicals attached to the double bond. The extent of this displacement from the arrangement of electrons in the methane molecule, we believe to be responsible for the larger energy content of ethylene derivatives. Furthermore, while this displacement in the case of the ethylene derivatives cited is about 13 kgm. cal. per mole, that may merely be due to the fact that the experimental error of determination of heats of combustion may be too large for the determination of such small differences, which may exist if the second pair of electrons is held in the second instead of the first energy level of figure 1, or even in the third, etc. At any rate, this concept implies that this second pair of electrons may be considerably displaced, but still shared in outer energy levels from one carbon atom, and displaced to some extent (as represented for instance by an amount of energy equivalent to 13 kgm. cal. which amount of energy is required to displace these electrons from their "methane" energy level arrangement) from the other "normal" valence energy level of the other. However, the extent of this latter displacement may vary considerably, depending upon the radicals attached to the carbon atoms, so that we may have a number of gradations of double bonds, a fact which will naturally manifest itself in the ease with which various double bonds will absorb reagents.

Postulate IV. The relative position of the second pair of valence electrons of the double bond depends upon the nature of radical attached to it in such a way that they are always on the carbon atom

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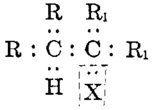
[8] This assumption is made for the sake of simplicity and also because there are no data which compel us to think differently. This assumption could, however, be verified if we had some data on the rate of addition of reagents to these electromers.

opposite to that carrying the most electronegative radicals. We were led to this assumption from the facts described in the paper of Kharasch and Marker, namely that the substitution of an electronegative phenyl radical for a hydrogen atom in the methyl group decreased the electronegativity of the radical, i.e., the fact that the methyl radical is more electronegative than the benzyl radical. Secondly a study of the addition reactions of simple ethylene derivatives containing decidedly electronegative radicals led us also to the postulate stated above. In speaking of relative electronegativity of radicals we make use of the table of electronegativity of organic radicals given in the paper of Kharasch and Marker and some general principles in regard to electronegativity of radicals which we shall develop later.

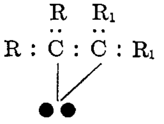
Postulate V. Alkyl and aryl radicals are more electronegative than a hydrogen atom. This is not, strictly speaking, correct, for while it applies to simple radicals, it is conceivable that there are radicals less electronegative than hydrogen. Thus indications are that the radical CH_2Br or any other radical CH_2X where X is a strongly electronegative radical may be almost equal in electronegativity to the hydrogen atom. However, in the absence of a table of electronegativities including the hydrogen atom, we shall allow this to stand. Elaborations as to types of radicals which are less electronegative than hydrogen are given later in the paper.

Postulate VI. In the formation of an unsaturated derivative from an alkyl halide it is assumed that the halogen is removed, taking with it the pair of valence electrons and the hydrogen drops off to maintain the electrical neutrality of the molecule, thus:

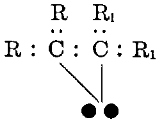


$$\begin{array}{ccccccc} & & R & & R_1 & & \\ & & \ddot{} & & \ddot{} & & \\ R & : & C & : & C & : & R_1 \\ & & \ddot{} & & \ddot{} & & \\ & & H & & \boxed{X} & & \end{array}$$

This gives Structure I for the unsaturated molecule,



Structure I



Structure II

which may or may not be the stable structure for this unsaturated derivative (see Postulate III). The following three alternatives are possible.

1. If the radical R_1 is decidedly more electronegative than the radical R the form given above (Structure I) would represent a stable structure.
2. If the radical R is decidedly more electronegative than the radical R_1 the following structure would probably be the structure of the compound, under the conditions that unsaturated derivatives are ordinarily prepared, namely, Structure II.

This of course represents a rearrangement of a pair of valence electrons induced by the strain in the molecule, and would occur only if, as stated, the radical R is very much more electronegative than the radical R_1.

3. If the radical R is only very slightly more electronegative than the radical R_1 the compound of Structure I may exist, but when the molecule is subjected to the action of heat, or light, it will tend to rearrange to the most stable form, Structure II. It is among this class of compounds that one should presumably look for electro-isomerism, and where the isolation of electromers should be the easiest.

Postulate VII. In case the radicals attached to the carbon atoms of the double bond are all different the same principles apply as were developed for compounds in which two radicals of the same type were assumed to be attached to a carbon atom.

COMPARISON OF THE PARTIAL POLARITY HYPOTHESIS WITH THOSE OF LEWIS, CAROTHERS AND LUCAS

a. Carothers' hypothesis

Carothers' able paper (15) is an attempt to interpret some facts of organic chemistry by means of the Lewis-Langmuir concepts involving the octet theory. It is impossible, however, by using his premises to predict the addition reactions at the double bond.

b. Lucas' extension of the Lewis hypothesis

Lucas and his collaborators (19) follow closely in all the essentials the Lewis theory and attempt to adduce experimental evidence in favor of that hypothesis. Therefore, in discussing the work of these authors we will at the same time get a glimpse at the validity of the Lewis hypothesis.

As mentioned above, we fully agree with Lucas' criticism of the Cuy hypothesis, but we believe that the facts advanced by Lucas are not entirely valid, which would also invalidate the hypothesis advanced by Lucas and collaborators. These investigators reason on the basis of electron displacement, that if a molecule of 2-pentene is treated with HBr, the reaction should yield 3-bromopentene, since the methyl group exerts a stronger pull on electrons than ethyl group. The basis of this argument according to these authors is found in the fact that the methyl radical must exert a stronger attraction for the electrons than the ethyl radical for the ionization constant K_a for acetic acid is larger than K_a for propionic acid. Lewis also states "hydrogen is more negative than a methyl radical, but more positive than a phenyl radical. Methyl alcohol is a weaker acid than water, phenol is a stronger acid."

c. Validity of the concept of electron displacement

1. Ionization constants of acids. 2. Addition of unsymmetrical reagents to compounds containing double bonds. If rigidly applied the above argument leads nowhere. Thus formic acid should then be a weaker acid than benzoic acid while in reality it is a much stronger acid, the ionization constants being K_a formic 2.14×10^{-4} and K_a benzoic 6.6×10^{-5}. However, while this is a serious objection and would invalidate this method of determining electronegativity of organic radicals, yet we wish to raise a few other objections to the method, for we admit that by a superficial examination one may be tempted to draw such a conclusion. Unfortunately, the data at hand do not allow one to draw far-reaching conclusions. Thus, an examination of the data of the ionization constants of the aliphatic acids shows sufficient variations to invalidate any conclusion drawn from it. The data merely indicate that ionization is molecular function. This latter property we believe to be shown more strikingly by a consideration of tables 1 and 2. Thus, in table 1 we note that there is a definite effect of the halogen atom in increasing the ionization constant of the acid, and that the effect diminishes rapidly, and the drop is sudden after the α carbon atom, so that when the halogen is on β or γ carbon atoms the effect is relatively slight. These facts we admit to be in perfect agreement with the Lewis theory. However, a rigorous application of this principle to the aromatic acids, without assuming that it is the entire radical, *R*, rather than the halogen alone which

TABLE 1

Ionization constants, K_a for halogen acids

	Cl	Br	I
α-halogen propionic acid	1.6×10^{-3}	1.08×10^{-3}	9×10^{-5}
β-halogen propionic acid	8.6×10^{-5}	9.8×10^{-5}	
α-halogen butyric acid	1.5×10^{-3}	1.06×10^{-3}	
β-halogen butyric acid	9×10^{-5}		
γ-halogen butyric acid	3×10^{-5}	2.62×10^{-5}	
δ-halogen valeric acid	1.91×10^{-5}	1.91×10^{-5}	1.7×10^{-5}
α-chloro crotonic acid	7.2×10^{-4}		
β-chloro crotonic acid	1.44×10^{-4}		
α-chloro isocrotonic acid	1.58×10^{-3}		
β-chloro isocrotonic acid	9.47×10^{-5}		

TABLE 2

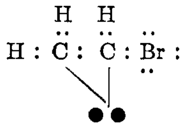
Ionization constants K_a of some organic acids

	Cl	Br	I
Halogen benzoic acid			
ortho	1.32×10^{-3}	1.45×10^{-3}	1.32×10^{-3}
para	9.3×10^{-5}	6.6×10^{-5}	1.36×10^{-4}
meta	1.55×10^{-4}	1.37×10^{-4}	1.63×10^{-4}
	ORTHO	META	PARA
Toluic acid	1.25×10^{-4}	5.2×10^{-5}	4.5×10^{-5}*

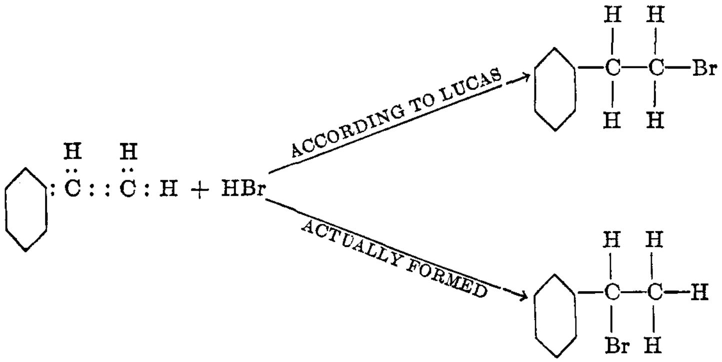
* The values vary from 5.2 to 3.8..

increases dissociation, would predict that in the case of the halogen benzoic acids the effect in increasing dissociation should be very slight since in the ortho acids the halogen is on the β-carbon atom. In reality the increase in strength of the acid corresponds to the increase observed in the aliphatic series when the halogen is on the α-carbon atom. Furthermore, the replacement of a hydrogen atom by a methyl group in the aliphatic series decreases the ionization of the acid, while when the methyl group replaces a hydrogen in the ortho position of benzoic acid, the strength of the acid is increased, while the same replacement of the hydrogen in the para and meta positions decreases the strength of the benzoic acid. The only conclusion that one may draw from these data is that ionization is a molecular effect, and that in our imperfect knowledge of the effect of the solvent in causing ionization and even the significance of our measurement, no reliance should be placed on this particular method of reasoning and that it is not permissible to draw conclusions in regard to the relative electronegativity of organic radicals from these premises.

Furthermore, it can be shown by a consideration of a number of organic addition reactions that this principle is not applicable. Thus, it is well known, that when vinyl bromide is treated with HBr, ethylidene bromide is formed. We repeated that reaction, and while we found the reaction to proceed slowly, yet the product formed was 99 per cent ethylidene bromide. Now, vinyl bromide according to Lewis and Lucas and collaborators should have this structure,



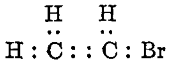
since bromine is more electronegative than a hydrogen. This compound should then add HBr to give ethylene dibromide—a conclusion in complete disagreement with the experimental fact. Furthermore, according to Lewis' concept since phenyl is more electronegative than hydrogen, styrene should add HBr to give phenyl ethyl bromide, again in complete disagreement with the experimental fact, for the product formed is proven to be bromo ethyl benzene



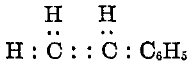
Similarly, in the case of β-chloro propylene the theory of Lewis as elaborated by Lucas would predict that this product should add HI to give $CH_2I\text{-}CHCl\text{-}CH_3$ while the product recorded in the literature is $CH_3\text{-}CClI\text{-}CH_3$.

Perhaps these facts in themselves are sufficiently illustrative that the fundamental concept of electron displacement as developed by Lewis and extended by Lucas and collaborators is not valid and that it is impossible to set up a theory on the basis of these concepts which will adequately cover the data and help us systematize the known facts.

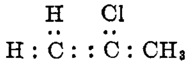
However, the examples cited fit very readily into the theory of partial polarity. Thus, writing down the examples which disagree with the Lewis theory,

1. 

$$\mathrm{H} : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : \mathrm{Br}$$

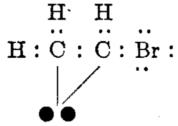
2. 

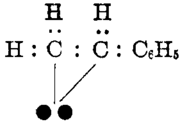
$$\mathrm{H} : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : \mathrm{C_6H_5}$$

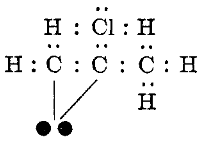
3. 

$$\mathrm{H} : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : : \overset{\mathrm{Cl}}{\ddot{\mathrm{C}}} : \mathrm{CH_3}$$

and applying our postulates we are able to assign at once the position of the second pair of valence electrons and thus predict the course of the addition at the double bond. Thus, in examples 1, 2 and 3, each of the radicals attached to the double bond is more electronegative than the hydrogen atom, then according to Postulate IV, the second pair of valence electrons would be found on the carbon atom opposite the one carrying the most electronegative radical. The following formulas would, therefore, represent the polarity at the double bond and it may be readily noticed that the predicted addition reactions of these molecules are in conformity with the experimental data.

1.


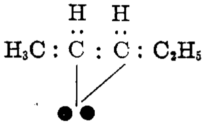
2.


3.


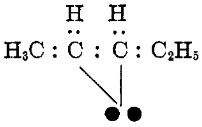
ELECTRO-ISOMERISM OF ETHYLENE COMPOUNDS

a. The existence of electromers of 2-pentene

There is one fact, however, which is advanced by Lucas and Moyse which is in disagreement with our theory, namely the addition of HBr to 2-pentene to give 22 per cent of 2-bromopentane and 78 per cent of 3-bromopentane. According to these authors the molecule of 2-pentene should have an electronic structure as represented by Form 1,

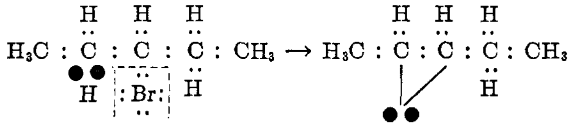


Form I



Form II

for a methyl radical is more electronegative than an ethyl radical and will attract the valence electrons toward itself. According to our theory, however, since methyl is more electronegative than ethyl, Form II should represent the position of the second pair of electrons (see Postulate IV). The experiment performed by Lucas and Moyse indicated, however, that 78 per cent of 3-bromopentane was formed and only 22 per cent of 2-bromopentane, more in agreement with Formula I than II. We repeated Lucas and Moyse's work and found their results to be entirely correct. A careful analysis, however, of Lucas and Moyse's method of preparing the 2-pentene revealed the fact that since the 2-pentene is prepared from 3-bromopentane the following might represent the course of the reaction:



$$\mathrm{H_3C : \overset{H}{\underset{H}{\ddot{C}}} : \overset{H}{\underset{:\ddot{Br}:}{\ddot{C}}} : \overset{H}{\underset{H}{\ddot{C}}} : CH_3 \longrightarrow H_3C : \overset{H}{\ddot{C}} : \overset{H}{\ddot{C}} : \overset{H}{\underset{H}{\ddot{C}}} : CH_3}$$

The bromide ion is removed by the alcoholic potassium hydroxide, the hydrogen ion drops off to maintain the electrical neutrality of the molecule and unsaturated derivative of Form I would be produced. Also, since the methyl radical is only slightly more electronegative than the ethyl radical, the rearrangement to Form II, the most stable condition would only be a slow one, and that might account for the addition of HBr as observed by Lucas and Moyse, and confirmed by us. The possibility then suggested itself that, by applying a "strain" to the system, the transition might be expedited. From that it was reasoned that perhaps heat might transform the 2-pentene of Form I into Form II. Accordingly, the 2-pentene was prepared exercising the most scrupulous care, and the work of Lucas and Moyse checked repeatedly, using a Zeiss dipping refractometer (which reduced the error of observation from 8 to 3 per cent) and the conditions studied which might have had an effect on the values obtained by Lucas and Moyse. Table 3 indicates, for instance, that the percentage of HBr in the acetic acid mixture is of small consequence, and that once the procedure employed by Lucas and

Moyse is followed faithfully entirely reproducible results are obtained.

There was no question, therefore, about the validity of Lucas and Moyse's observation and, furthermore, it indicated that we were dealing with the same compound. However, when the xylene solution containing the pentene was heated to 100° for eight to sixteen hours, and the material then worked up as before different results were obtained as illustrated in table 4. This difference is of course, beyond our experimental error, and furthermore, in many cases the two pentenes (heated and unheated) were recovered from the xylene solutions, in which they were kept, and worked up side by side, and invariably the 2-pentene which had been heated gave us a larger quantity of 2-bromo derivative than the unheated pentene.

TABLE 3

Checks on Lucas' and Moyse's work

NUMBER	REFRACTIVE INDEX	2 BROM COMPOUND	3 BROM COMPOUND	ACETIC ACID	HBr
		per cent	*per cent*	*grams*	*grams*
1	1.44371	22	78	60	43
2	1.44371	22	78	90	65
3	1.44371	22	78	84	80
*	1.44366	23	77	40	39

* Pentene subjected to five distillations before bromide was made.

TABLE 4

Pentene heated to 100°

NUMBER	INST. READING	REFRACTIVE INDEX	2 BROM COMPOUND	3 BROM COMPOUND	TIME
			per cent	*per cent*	*hours*
1	79.1	1.44346	32	68	16
2	79.0	1.44343	32	68	16
3	79.1	1.44346	32	68	8
4	78.8	1.44337	34	66	16

Our next task was to ascertain the effect of temperature and light. The tubes containing the xylene solution of 2-pentene were immersed in a glycerin bath and the latter exposed to light from a Mazda lamp. Table 5 indicates that temperatures of 50–60° had very little effect.[9]

Further investigation in regard to the existence of the two electromers of 2-pentene consisted in an endeavor to change the proportion of the two forms (as judged by the different amounts of the two bromo derivatives formed when HBr is added to the mixture) by the use of ultra-violet light. The result of those

TABLE 5

Pentene subjected to various temperatures in presence of light

NUMBER	INST. READING	REFRACTIVE INDEX	2 BROM COMPOUND	3 BROM COMPOUND	TIME HEATED	TEMPERATURE	SOLVENT	ADDED SUBSTANCE
			per cent	*per cent*	*hours*			
1	80.2	1.44377	22	78	8	50–60°	Xylene	
2	79.3	1.44351	29	71	14.5	145–160°	Xylene	
3	79.1	1.44346	32	68	8	90–100°	Xylene	
4	79.3	1.44351	29	71	8	80–90°	Xylene	Bromine*
5	79.3	1.44351	29	71	8	80–90°	None	

* A trace of bromine added to the pentene before heating had evidently no effect on the proportion of the two electromers formed.

TABLE 6

Pentene subjected to ultra-violet light

NUMBER	INST. READING	REFRACTIVE INDEX	2 BROM COMPOUND	3 BROM COMPOUND	TIME EXPOSED	LENGTH OF TIME AFTER EXPOSURE UNTIL BROMIDE WAS MADE
			per cent	*per cent*	*hours*	
1	79.2	1.44348	30	70	6	Two days
2	78.5	1.44329	38	62	8	
3	78.5	1.44329	38	62	8	Two to four hours
4	78.1	1.44318	42	58	16	Two to four hours
5	77.4	1.44298	49	51	29	Two to four hours
6	78.4	1.44323	40	70	29	Three days
7	78.5	1.44327	38	62	29	Two days

---

[9] Whether the lower yield at 145°–160° is significant is difficult to decide. The difference is well within the limit of the error of the experiment. Yet, the yields of the 2-Bromo derivative were consistently lower at higher temperatures. This point is under investigation at the present time.

experiments was a large change in the proportion of the two electromers[10] (table 6).

In examining table 6 it is important to bear in mind that the technique of HBr addition was not varied in any way from that employed when we were repeating the work of Lucas and Moyse. The only difference between the two experiments was that in one case the 2-pentene was exposed to ultra-violet light and some hours later HBr added to it under exactly the same condition as called for by Lucas and Moyse, the outcome of the addition, however, being entirely different. We attribute this difference to the fact that under the action of ultra-violet light the proportion of the two electromers was changed. The physical side seems also to lend some support to this view. Thus, in one set of experiments a large quantity of 2-pentene was put into a quartz tube and the gross absorption spectra determined. The 2-pentene was then exposed to the action of ultra-violet light and at stated intervals of eight, sixteen and twenty-nine hours, the absorption spectra determined again and at the same time samples were withdrawn and treated with hydrogen bromide. The absorption spectra work was only qualitative in nature, but a more quantitative study is under way. The absorption spectra work was carried out for us by Dr. B. H. Carrol of the Bureau of Standards, who has most graciously furnished us with the following report:

"The material said to be β-amylene was submitted with the request that the absorption spectrum be examined before and after exposure to ultra-violet radiation for varying lengths of time, as it was hoped that there would be a shift in absorption corresponding to the change in the relative amounts of the electromers in the sample. The sample was too volatile and too limited in amount to permit transfer to and from a cell, and the exposures covered a period of five days. It was, therefore, possible only to make approximate determinations of the

---

[10] We believe this to be the first instance where the effect of ultra-violet light on a substance containing a double bond has been proved to consist merely in the shift of the relative position of electrons with respect to the two carbon atoms. This notion has some far-reaching possibilities particularly with regard to the effect of ultra-violet light on vitamin D (Ergosterol). The relationship of our findings to vitamin D potency is under investigation by one of us.

absorption limit after each period of exposure. The tube containing the sample was used as a condenser to focus the radiation from a mercury arc on the slit of a Fery quarts spectrograph; for each determination three exposures of varying length were made with the tube in place, and three with the bare arc. The development of the films was comparable in all cases. The results given are based merely on visual observation of the lines.

"The method used permits only the statement that a shift in the limit of absorption to the longer wave lengths has been produced by exposure. This indicates an irreversible change in the composition of the sample; since, applying Le Chatelier's principle, an equilibrium should be shifted in the direction of decreasing absorption when the shift is due to absorption of radiant energy."

TABLE 7

TIME OF EXPOSURE	LONGEST WAVE LENGTH COMPLETELY ABSORBED	SHORTEST WAVE LENGTH TRANSMITTED	LONGEST WAVE LENGTH AT WHICH ABSORPTION CAN BE DETECTED	2 BROM COMPOUND	3 BROM COMPOUND
hours	Å	Å	Å	*per cent*	*per cent*
0	2753	2804	3028	22	78
8	2753	2804	3139	38	62
16	2857	2894	3663	42	58
29	2926	2968	3663	49	51

The last two columns of table 7 have been added by us in order to indicate that chemically, as judged by proportion of the two bromides formed when HBr is added to the substance, the 2-pentene has been undergoing a change when exposed to the action of ultra-violet light. We might add that we are inclined to interpret the data on addition reactions where two products are formed by the addition of a reagent to a substance containing a double bond, as arising only from the existence of two distinct electromers of that substance.

b. Does heat or ultra-violet light effect a change in the position of the double bond?

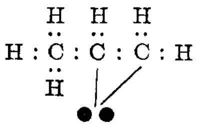
In order to prove conclusively that Electromer II produced from I is not 1-pentene, i.e., that heating the substance in an inert solvent did not shift the double bond to position–1, the two products were treated separately with bromine and the dibromides thus formed were compared. As shown in the experimental part (to be published elsewhere) there was not the slightest difference between the compounds thus formed—the dibromides agreeing perfectly in their indices of refraction, boiling point and density. We may safely assume then that heating did not shift the position of the double bond, but merely shifted the valence electrons in the sense previously discussed.

c. *Are the electromers cis-trans isomers?*

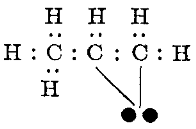
It is readily noticed that 2-pentene may exist in two forms, cis and trans. It may, therefore, be argued that the two electromers are cis-trans isomers. The data at hand do not allow one to draw such a far reaching conclusion. For that would imply that cis-trans isomers would add an unsymmetrical reagent in a different manner. The fact that the bromine addition products are the same would argue against such a conclusion. However, bromine is a poor reagent for such a purpose, and the oxidation of these electromers with permanganate—a reagent which is less likely to cause shifts from cis to trans is now being studied.

d. *Pertinent remarks regarding isolation of other electromers*

As previously discussed, the isolation of electromers of the type indicated should be possible whenever the radicals attached to the carbon atoms of the double bond are very close in electronegativity. However, if there is a great deal of difference in their electronegativity, then, even though we may attempt the preparation of electromers by eliminating the groups in the proper order, the rearrangement into the stable electromer will take place very rapidly. Thus, we attempted to prepare the two theoretically possible electromers of propylene by elimination of HBr from normal and isopropyl bromides respectively.



Electromer I



Electromer II

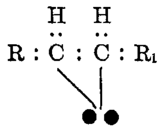
However, the addition of HBr to the propylenes prepared by these methods resulted under the experimental conditions, approximating those that we employ for the two pentenes, in the formation of isopropyl bromide exclusively, a fact which tends to show that although Electromer I of propylene was undoubtedly formed, it rearranged itself to II very quickly, due to the large difference in electronegativity between methyl group and the hydrogen atom.[11]

Similarly, in the case of styrene one would not expect to isolate the two possible electromers under conditions ordinarily employed in the laboratory, for the difference in electronegativity between the two radicals phenyl and hydrogen, is so large that the unstable electromer would rearrange very rapidly into the other form.

EXTENSION OF THE THEORY OF PARTIAL POLARITY TO ALL TYPES OF ETHYLENE DERIVATIVES

a. Predictions regarding addition of unsymmetrical reagents to ethylene compounds and criteria thereof

The directed addition reactions at the double bond may be predicted by making use of the postulates given, once the relative electronegativities of the radicals have been definitely established, particularly in cases where the effect of two radicals in displacing the valence electrons of the double bond is in the same direction. Thus, if in the molecule:



$$R : \overset{H}{\ddot{C}} : \overset{H}{\ddot{C}} : R_1$$

the radical *R* is strongly electronegative, while R_1 is very weakly electronegative, the position of the valence electrons of the double bond would be as indicated, and only one product would result from the addition of halogen acid. However, if both radicals *R* and R_1 are electronegative then the position of the

---

[11] In our analysis of the propyl bromides formed we employed the index of refraction. A preliminary examination of the index of refraction of known mixtures of propyl and isopropyl bromides indicated that the index of refraction was a linear function of composition.

second pair of valence electrons would depend upon the relative positions of the radicals R and R_1 in the table of electronegativity, i.e. they would be closer to the nucleus of the carbon atom carrying the least electronegative radical. However, even though that form would predominate the possibility is that the other form would also exist, and two products should be formed, when HBr is added to such a molecule.[12]

The main difficulty of predicting all types of addition reactions is as previously mentioned, due to our ignorance of the relative electronegativity of organic radicals. However, with two simplifying assumptions it becomes possible to reconcile our addition reactions at the double bond with the facts actually known. The first assumption is that any alkyl or aryl radical is more electronegative than hydrogen. Secondly, that if a carbon atom has strongly electronegative radicals attached to it that group may become equal or lower in electronegativity than the hydrogen atom. It is among such compounds that one may find a large number of examples of electro-isomerism, and it is among such compounds that we find that experimental conditions will determine to a large extent the relative amounts of the two compounds which are always formed.

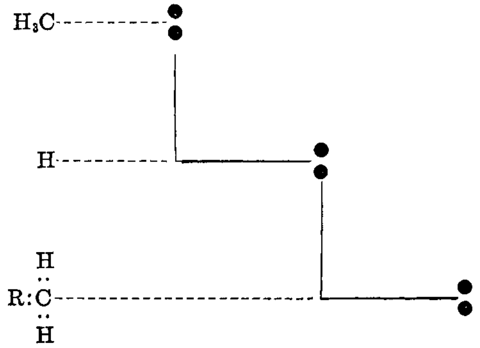
The first assumption is self evident—it means that such groups as phenyl, methyl, ethyl or naphthyl are more electronegative than the hydrogen atom, although it is quite conceivable that an overlapping may occur somewhere, for instance in the case of long-chain aliphatic radicals. In the second assumption we merely imply that since an electronegative radical attached to a methyl carbon atom decreases enormously the electronegative character of the group, that it would tend to put us on the other side of the electronegativity of the hydrogen atom.

[12] Once this view is adopted it becomes possible to compare the relative electronegativity of such radicals as phenyl and bromine. The literature records that the product of the reaction of bromo-styrene with HBr gives styrene dibromide. Our own experience with this reaction led to the same result. This would seem to indicate that the phenyl radical is more electronegative than a bromine atom. Work is under way at the present time to determine the relative electronegativity of a phenyl radical with a chlorine and fluorine atom, by studying the addition reactions of halogen acid to the corresponding styrene halogen compounds.

Thus, while the phenyl radical, a bromine, or chlorine atom, or an hydroxyl group or oxygen atom are individually more electronegative than a hydrogen atom, when they become attached to a methyl carbon atom as for example in the radical benzyl or bromo methyl or chloro methyl they make those groups either less electronegative than hydrogen, or almost equal in electronegativity to the hydrogen atom. The general idea of this concept is conveyed in table 8.

TABLE 8

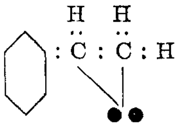
Possible electronegativity of radicals with respect to hydrogen

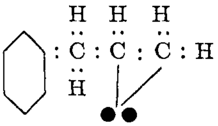


Where *R* is a strongly electronegative radical

In addition reactions at the double bond, therefore, such groups as benzyl or bromo or chloro methyl, carbonyl, or carboxyl when attached to a carbon atom of the double bond should have an effect opposite to the one that the phenyl radical or bromine atom have when attached to the same carbon atom of the double bond. The prediction would be that in vinyl bromide the bromine atom forces the second pair of electrons on to the opposite carbon atom. However, in allyl bromide, the position of the pair of valence electrons will depend upon the relative electronegativity of the two radicals, hydrogen atom and bromo methyl radicals. These radicals are quite close together in the electronegativity series. According to our postulate, however, since the hydrogen atom is slightly more electronegative, the second pair of electrons of the double bond will be closer to the carbon atom carrying the bromo methyl group than the carbon atom carrying the hydrogen atom. The system, however, will be a labile one, and capable of change by the application of heat or other forms of energy—such as light.

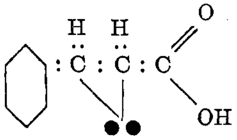
Our experiments confirmed these suppositions, for when vinyl bromide and allyl bromide were treated with HBr they gave only ethylidene bromide and 1,3 dibromo propane (when the addition was carried out in light). It was to be expected also from these considerations that while styrene adds HBr to give 1-bromo ethyl benzene, the molecule β-phenyl propylene containing a group attached to a carbon of the double bond which is presumably less electronegative than hydrogen should have this structure:


Styrene


β-Phenyl propylene

and therefore add hydrogen bromide to give γ-phenyl normal propyl bromide. Experiment confirmed this prediction. However, since the bromide was not described in the literature, the product of the reaction was shaken with silver oxide. The alcohol obtained in this manner was γ-phenyl normal propyl alcohol.

Similarly, since the carbon atom of the carboxyl group has strongly electronegative atoms and groups attached to it, with the consequent displacement of all the electrons of the carbon atom into outer energy levels (Postulate I), the whole group is an exceedingly weak electronegative radical, weaker than the hydrogen atom. This would imply that if the carboxyl group and a bromine atom or a phenyl or methyl group are attached to the two carbon atoms of the double bond respectively, their effect would be in the same direction and only one product should result. In the case of cinnamic acid the electronic structure at the double bond would be, upon this hypothesis, the following:



the pair of valence electrons being completely over in the direction of the carbon atom next to the carboxyl, although they would still be shared in some outer energy levels of the carbon atom carrying the phenyl radical.

On the other hand, if the strongly electronegative radical and the carboxyl group are attached to the same carbon atom of the double bond their effect would be in the opposite direction, and we might expect two products. It is also among such compounds that one may look for the phenomenon of electro-isomerism.

b. Theoretical explanation of ease of addition of reagents by compounds containing double bonds

The halogens add to the double bond in the order of chlorine, bromine, iodine, while the reverse order holds for the halogen acids. This is easily accounted for on the basis of the general concept of the double bond represented in figure 2. For it is at once evident that while we may consider the first step in the absorption reaction of a halogen acid to consist in the addition of the hydrogen ion to the displaced electrons, before the addition is complete, the electrons from the halogen must be pulled into the inner energy levels of the carbon atom which is deficient in electrons. Naturally it requires larger quantities of energy to accomplish this in the case of the chloride ion, than in the case of the bromide and iodide ions. It follows also that the more electronegative the radicals *R* the farther out will be the electrons which the carbon atom of the double bond will be capable of holding—the smaller would be the amount of energy necessary to pull the electrons from the halogen, and the greater should be the ease of addition. We believe this to be in harmony with the described experimental facts. Thus it is recorded that while ethylene does not add HCl, chloroethylene adds it readily. Other illustrations are available in the literature. However, it must be remembered at all times that ease of addition implies that the valence electrons of that carbon are more readily satisfied in outer energy levels and with a strongly electronegative halogen attached to it, the molecule should also decompose more readily. It is quite possible that in a good many cases where we state that the substance does not add a reagent, it may be due to the fact that while addition does take place, the decomposition of the molecule under the conditions of the experiment is exceedingly rapid, and that under another set of conditions the molecule may actually be isolated.[13]

SUMMARY

A comparison is made between the various electronic hypotheses which have been advanced to interpret the directed addition reactions of ethylene derivatives. It is shown that the hypothesis of partial polarity of the double bond[14] covers the existing data more satisfactorily than any of the other theories. The application of this hypothesis to thirty-five ethylene addition reactions recorded in the literature gives results in conformity with the experimental facts.

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[13] Note, for instance that at low temperatures triphenyl ethylene adds bromine, but as soon as the temperature rises HBr is evolved. The net result is the replacement of a hydrogen atom by a bromine atom, but it is significant and in accord with our theory that the substitution takes place through addition. The instability of the molecule is also in agreement with our predictions.

[14] From the standpoint of the hypothesis developed in the paper one can not agree with the arguments and deductions of Gilman and Peterson (J. Am. Chem. Soc. **48,** 423 (1926) with regard to the non-existence of a polar bond in ethylene derivatives. The non-addition of a reagent (in this case the Grignard reagent) has no bearing to polarity in the molecule—but may be due to unfavorable energy change if a combination of that type took place. Furthermore the experiment as designed did not take into account the true polar ionization of the Grignard reagent.

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