

THE EFFECT OF HEAT AND ULTRA-VIOLET LIGHT ON UNSATURATED
COMPOUNDS AND THE THEORY OF ELECTROISOMERISM

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INTRODUCTION

This work was commenced because a paper published¹ by Lucas and Moyse contained experimental facts that were directly contradictory to the theory of partial² polarity . This work was pursued with the idea in mind of extending our knowledge of the position of electrons at points of unsaturation in the carbon chains of unsaturated hydrocarbons, and to obtain information in regard to the changes brought about in the geometrical positions of the groups connected by double bonds by the application of energy.

REVIEW OF PREVIOUS WORK

Older Theories

1. Kekule's Conception of the Double Bond

An extensive study of the addition taking place at the double bond has been made in the past, and the theoretical speculations offered to explain the mechanism of these reactions have undergone a gradual

¹

Electron Displacement in Carbon Compounds. J. Am. Chem. Soc. 47, 1459, (1925).

²

Kharasch and Sher. The Electronic Conception of Valence and Heats of Combustion of Organic Compounds. J. Phys. Chem. 29, 625, (1925).

evolution from the original ideas of Kekule³ to the modern conceptions advanced by Lewis⁴ and extended in⁵ their applications to organic reactions by Kharasch . Kekule conceives the matter in the following way: "in any chemical action the two reacting molecules are first drawn together by the mutual exercise of chemical affinity and then ultimately become attached to each other. In this closer association, individual atomic attractions make themselves felt, with the result that atoms which had previously been present in two different molecules come into very close proximity. Such rearrangements may finally lead to the disruption of the whole complex and the formation of entirely new molecules". He also postulated that the four carbon valencies were in one plane and said that a single bond corresponded to one collision per unit time and that a double bond corresponded to two collisions between carbon atoms per unit time. But this idea failed to stand criticism, principally due to the fact that it could not explain the existence of the four tartaric acids. He recognized the fact that where double bonds occurred chemical activity was indicated, and he assumed

³
Theories of Organic Chemistry. Henrich, page 168.

⁴
The Atom and the Molecule. G. N. Lewis. J. Am. Chem. Soc. 38, 762, (1916). Valence and Structure of Atoms and Molecules by G. N. Lewis.

⁵
loc. cit.

that free valencies were present in unsaturated compounds. The fact that all attempts to prepare methylene resulted in the formation of ethylene led him to the assumption that valencies which were set free in the formation of unsaturated compounds mutually saturated each other, thus giving rise to double and triple bonds between atoms. But the formulas used to express these ideas were construed to mean something different from that which they were intended. That is, in the case of $\text{CH}_3\text{-CH}_3$, $\text{CH}_2\text{=CH}_2$ and $\text{CH}\equiv\text{CH}$, the symbols were construed to suggest a greater stability for acetylene and ethylene than for methane which was directly contradictory to the facts.

II. Baeyer's Tension Theory

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A. von Baeyer in his so-called "tension theory" was the first to offer a rational explanation of the gradually decreasing stability observed in the compounds containing double and triple bonds. Baeyer based his tension theory on van't Hoff's assumption that the four valencies of carbon were directed toward the four corners of a tetrahedron at the center of which the carbon atom was assumed to be located, the normal angles of valencies being $109^\circ 28'$. In the case of the double and triple bonds the valencies were

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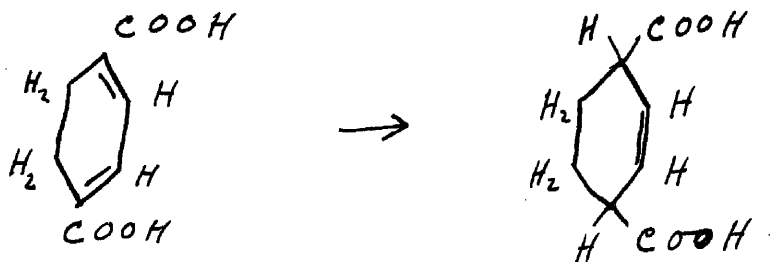
Ber. 18, 2277, (1885); 23, 1275 (1890).

assumed to be bent out of their normal angles and this would exert a tension which would make these molecules less stable than those in which the valencies were at their normal angles.

III. Thiele's Hypothesis⁷

Later Thiele pointed out that while it was possible to explain the behavior of substances possessing a single pair of double or triple bonds by means of the theories mentioned above, it was impossible to interpret in the same manner the properties of substances possessing a conjugated system or two pairs of adjacent double bonds.

He points out that piperic acid, $\text{CH}_2(\text{O})_2\text{C}_6\text{H}_3\text{CH}=\text{CH}-\text{CH}_2\text{COOH}$, always gives as its normal reduction product⁸ hydropiperic acid, $\text{CH}_2(\text{O})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{COOH}$.⁹ Also in the case of dihydroterephthalic acid reduction causes the formation of a new double bond.

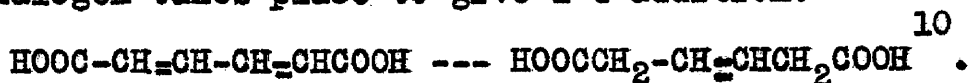


⁷
Ann. 306, 87, (1899).

⁸
R. Fittig. Ann. 152, 47; 172, 158; 216, 171; 227, 46, (1888).

⁹
Baeyer. Ann. 251, 271, (1889).

Also in the case of muconic acid, addition of hydrogen and halogen takes place to give 1-4 addition.



After collecting many examples both in the aliphatic and aromatic systems in which addition always took place in the 1-4 and never in the 1-2 or 3-4 positions as the older theories would postulate. Thiele¹¹ advanced his "Theory of Partial Valencies" to explain this 1-4 addition. He says that in the case of two unsaturated atoms, these atoms may be imagined as joined together by means of four valencies (in the case of double bonds) which have united to form a double bond, but in this union all four valencies are not mutually and completely saturated, since in the case of the second pair only a fraction of each unit of affinity is exercised in holding the two atoms together, while a residue of affinity is left free. To this residue of free affinity Thiele gives the name "partial valency". He represents it graphically in a chemical formula by means of a dotted line as $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$,
 $\text{O}=\text{N}$, $\text{N}=\text{N}$.

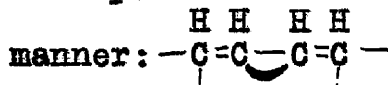
In the case of the addition of hydrogen to a conjugate system one would expect the simultaneous addition

¹⁰ Baeyer and Rupe. Ann. 256, 1, (1890).

¹¹ loc. cit.

of four hydrogen atoms to each of the four carbon atoms but observation has shown that only two hydrogen atoms add on, and these in the 1-4 and not in the 1-2 or 3-4 positions. This behavior led Thiele to postulate that the partial valencies on the 2 and 3 positions mutually saturate each other, combining to give a new kind of double bond between the respective atoms. Thiele calls this form of combination an "inactive double bond".

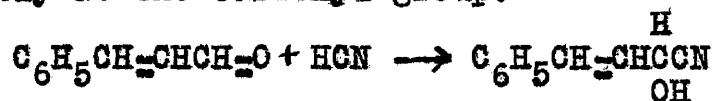
He represents this system of atoms in the following



Assuming the above to be true, the formation of symmetrical addition products may be accounted for. The adding atoms or groups will naturally attach themselves so as to neutralize the free residual affinities of the end carbon atoms. Since the adding atoms will require more affinity for saturation than is afforded by the partial valencies, addition will be followed by a rupture of the double bonds joining the pairs of atoms 1-2 and 3-4. The free affinities of 2 and 3 will then combine to form a double bond which will replace the inactive single bond between the central atoms.

Later work has shown that Thiele's theory will only hold in a small portion of cases. It holds in most instances for the addition of hydrogen but in the case of the addition of halogens it falls down in part and in the case of the addition of halogen acids, HCN,

HONH_2 , it is of very little value in predicting where the groups or atoms will add onto the conjugated system. In the case of the addition of HBr to $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ a mixture of products is obtained, the main product being $\text{CH}_2\text{BrCH}=\text{CHCH}_2\text{Br}$ and a smaller amount of the isomer $\text{CH}_2\text{BrCHBrCH}=\text{CH}_2$. In the case of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHC}_6\text{H}_5$ on addition of bromine a 96 per cent yield of 3-4 or 1-2 compound is obtained. In the case of the addition of HCN to cinnamic aldehyde the addition takes place completely at the carbonyl group.



These examples point out where Thiele's theory fails.

IV. Markownikoff's Rule for the Addition of

Halogen Acids

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Markownikoff made a study of the addition of halogen acids at the double bond and formulated the following empirical rule: "the halogen always goes to the carbon atom containing the least number of hydrogen atoms". But the literature shows many exceptions to this rule.



This reaction which the literature gives as shown above shows that the rule fails to predict the position at which the halogen will add.

12

Ann. 153, 256, (1870).

Newer Theories

There were no theories offered that were any improvement on Thiele's until recently when the electronic conception of valence has been applied to organic molecules.

I. Thompson's Corpuscular Theory

J. J. Thompson, the discoverer of the electron, was probably the first investigator to point out that the linkages between atoms in a compound were caused by a transfer of electrons, or as he called them corpuscles, in his Corpuscular Theory of Matter¹³.

Arrhenius had previously assumed that electrolytes were held together by electrical forces. But it was¹⁴ Helmholtz in his Faraday lecture of 1881 who first drew attention to the fact that if the atomic theory was correct therefore electricity must also be atomic in nature.

J. J. Thompson's hypothesis stated in his own words is as follows: "For each valency bond established between two atoms the transference of one corpuscle from the one atom to the other has taken place, the atom receiving the corpuscle acquiring a unit charge of negative electricity the other by the loss of a corpuscle acquiring a unit charge of positive. This

¹³

The Corpuscular Theory of Matter. J. J. Thompson. (1907)

¹⁴

Faraday Lecture. J. Chem. Soc. of London. (1881).

This electrical process may be represented by the producing of a unit tube of electric force between the two atoms, the tube starting from the positive and ending on the negative atom. There is, however, one important difference between the lines representing the bonds and the tubes of electric force. The lines used by the chemist are not supposed to have direction. On the electrical theory, however, the tubes of electric force are regarded as having direction starting from the positive and ending on the negative atom". This hypothesis supplements the structural formulas employed up to this time by giving the bonds direction.

II. Complete Polarity

A. Falk and Nelson's Interpretation of Thompson's Ideas

Falk and Nelson¹⁵ have built up a set of postulates around Thompson's ideas regarding the constitution of the atom. They assume that

1. each individual atom represents a close confederation of electrons and that they are in constant motion. If, by the action of physical or chemical forces, one or more electrons are separated from the atom, the latter receives a corresponding positive charge.

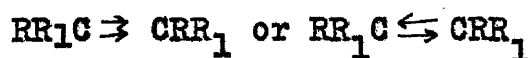
2. the atoms of the different elements differ from each other in the ease with which their electrons

dissociate.

3. the ability of an atom to enter into chemical combination depends upon its power to hold electric charges. A mono-valent atom is one which carries a unit charge of electricity, while a multi-valent atom is one which bears two or more such units, the number varying according to the valency of the element.

4. every chemical combination between atoms is accompanied by an exchange of electrons. To denote this change they use an arrow, $\longrightarrow$. The direction of the arrow is used to denote the direction taken by the electron in its passage from one atom to the other.

Falk and Nelson say the union of two carbon atoms by means of a double bond involves the transfer of two electrons from one carbon atom to the other, and that this may take place in either of two ways:



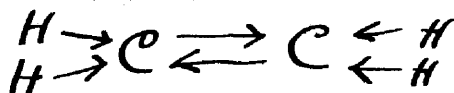
Of the two isomers theoretically possible in each case, one is more stable than the other. No isomerism has as yet been discovered in the case of substances belonging to the class of $R_2C=CR_2$ but Falk and Nelson assume that one of the two isomers is so unstable that it is transformed instantly into the other stable form. Compounds of the general formula $RR'C=CRR'$ are found in two isomeric modifications; but the theory would

predict the possibility of three isomers as:



They explain this discrepancy as in the preceding case by assuming one of the isomers to be so unstable that it cannot be isolated. These assumptions of unstable isomers is regarded as an evidence of weakness in the interpretations of Falk and Nelson.

They propose the following formula for ethylene:



In regard to this they write, "in those cases where one valence proceeds in one direction and one in the other, it is assumed that the electrons which are transferred are localized on the atoms, as otherwise the carbon atoms would become electrically neutral."

But this statement as Lewis¹⁶ says is admitting a weakness in the theory; for they may just as well say that a carbon atom has lost an electron in one part and gained one in another part and indicate it by vertical arrows as: $\begin{array}{c} \text{H} \rightarrow \text{C} \downarrow \uparrow \text{C} \leftarrow \text{H} \\ \text{H} \rightarrow \text{C} \leftarrow \text{C} \leftarrow \text{H} \end{array}$ Here, however, there is left no indication of a bond holding the two carbon atoms together.

B. Fry's Postulate of Negative Hydrogen

After this Fry¹⁷ published a number of papers in which he sponsored the idea of complete polarity in

¹⁶

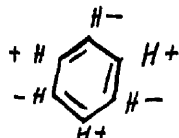
Valence and Structure of Atoms and Molecules. Lewis. page 73.

¹⁷

Z. Physik. Chem. 76, 385, 398, 591, (1911). 80, 29, (1912); 82, 665, (1913). J. Am. Chem. Soc. 34, 664, (1912); 36, 248, (1914).

organic compounds. Jones also supported this idea, while the latest attempt made to give impetus to the idea of complete polarity was contained in a paper published by Stieglitz¹⁹ in 1922.

In these papers attempts were made to show that it was possible to predict substitution at the double bond from the theory of complete polarity. Special effort was made to explain substitution in the benzene ring. Fry's interpretation involves the assumption of the presence of negative hydrogen atoms in benzene, as expressed in the formula



. He further

assumes only the positive hydrogen atoms react with such reagents as chlorine, bromine, etc. In criticizing this theory Stieglitz²⁰ points out the presence of negative hydrogen in the metallic hydrides as Na H and points out its powerful reducing action but states that "it would be illogical to consider that we have negative hydrogen in benzene without a trace of evidence of its presence, shown in reducing power or instability".

C. Stieglitz' Support of the Theory of Complete Polarity

Stieglitz, according to the theory of complete polarity, writes the formulas for monosubstituted

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J. Am. Chem. Soc. 36, 1268, (1914).

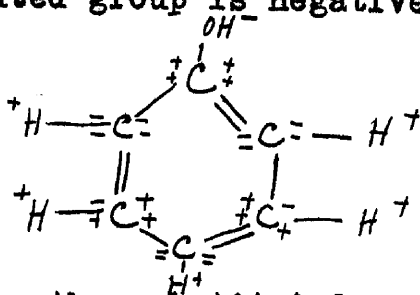
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J. Am. Chem. Soc. 44, 1293, (1922).

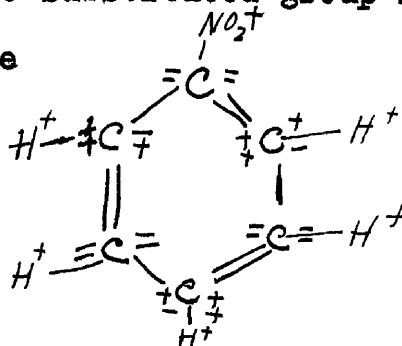
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loc. cit.

benzenes as follows: In the case of phenol where the substituted group is negative

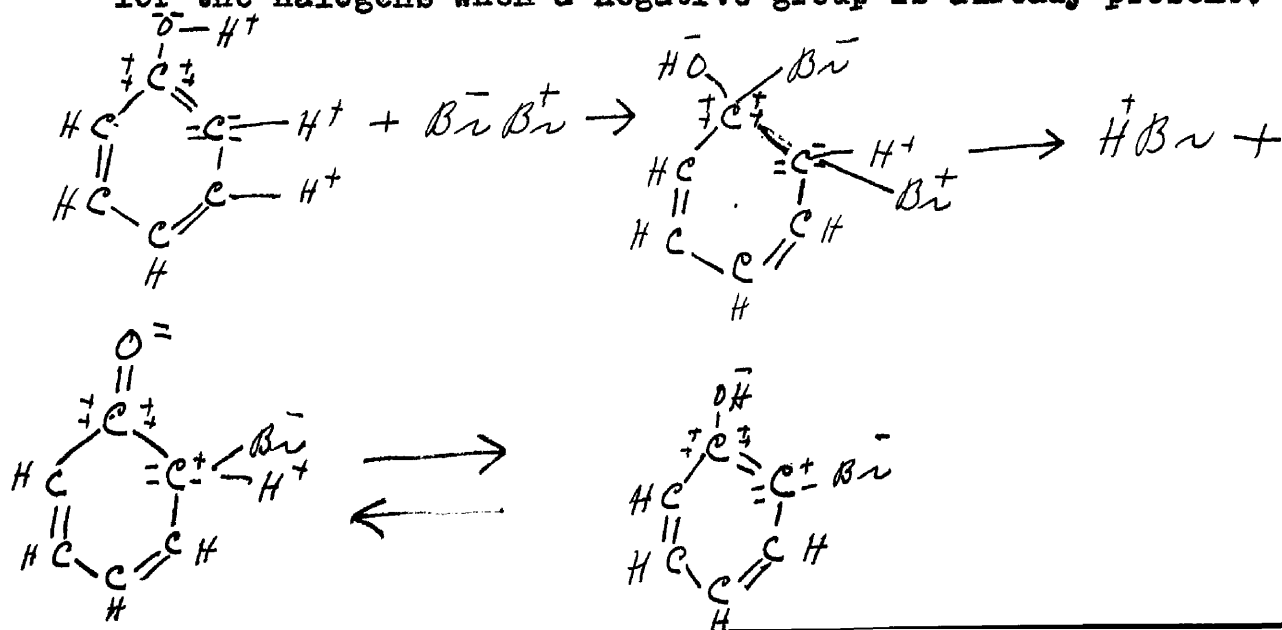


and where the substituted group is positive as in nitro benzene

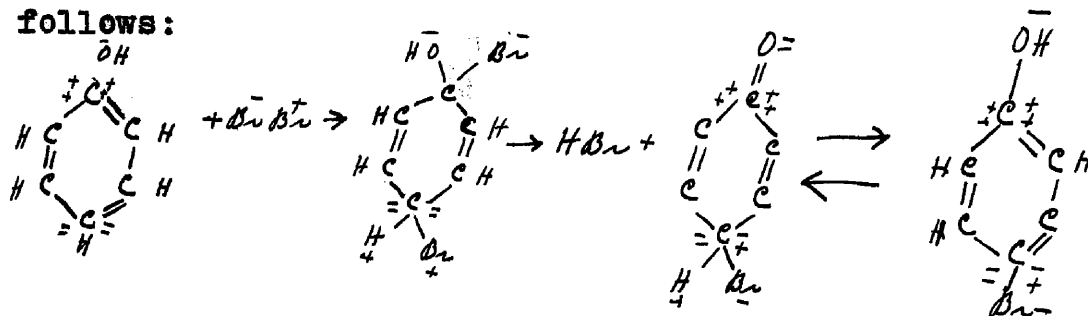


The hydroxyl being negative in the first formula would make the carbon atom it was attached to positive and it is assumed that the carbon atoms alternate first negative then positive until the carbon atom holding the hydroxyl is reached again. Thus giving a closed chain of alternating positive and negative carbon atoms.

Stieglitz gives the following equation in showing how the ortho substitution takes place in the benzene ring for the halogens when a negative group is already present.



In the case of addition in the para position Stieglitz falls back on Thiele's ideas of 1-4 addition to double bonds as a conjugated system exists in the benzene ring. He formulates the para addition as follows:



Stieglitz gives similar reactions for the addition that takes place in the meta position when the monosubstitution group is positive as in the case of nitro benzene.

21

Lewis gives the following criticism of Stieglitz' theory: "Stieglitz makes the ortho and para carbon atoms quadrinegative and the meta carbons bipositive. He thus assumes an enormous difference of six units of charge between meta carbons on the one hand and ortho or para carbons on the other. Such extreme polarization should produce strong effects upon the strength of a carboxyl hydrogen, it should affect very greatly the dissociation of hydrogen from the carboxyl

21

Valence and Structure of Atoms and Molecules. page 145

attached to the atoms in these positions. In the nitro and chloro benzoic acids we have an opportunity of testing these deductions. Chlorine orients in the ortho and para positions. The nitro group is the type of meta orienting groups. If Stieglitz' theory were correct we should expect the chloro benzoic acid to be a very strong acid in the meta arrangement, and very weak in the ortho and para. On the other hand we should expect ortho nitro benzoic acid to be very strong and meta nitro benzoic acid to be very weak. The fact is, though, that the dissociation constants of the meta and the ortho acids in each case are nearly the same". Stieglitz' theory in regard to the double bond in the benzene ring which requires such a large difference in the negativity of the carbon atom in the ortho and para positions, would demand complete addition of the entering constituent to the ortho and para positions or to the meta position. His examples of addition are discussed as if such is the case. He fails to point out the many cases where substitution takes place in all three positions as given below²².

1. Nitration of nitro benzene gives the following products: 18.5 per cent ortho compound, 80.2 per cent meta compound and 0.2 per cent para compound.

2. Addition of chlorine to bromo benzene: 41.5

per cent ortho compound, 6 per cent meta compound and 52.5 per cent para compound.

These examples of substitution show that Stieglitz' theory cannot be used to predict substitution in the benzene ring with any great degree of accuracy in most cases.

III. Theory of Alternating Polarity

Previous to the publication of Stieglitz' paper the theory of alternating polarity was brought forth by Cuy²³. Cuy only advanced his theory for carbon chain compounds of the aliphatic series and states that it is natural for the carbon atoms in a carbon chain to be alternately completely positive and negative or as completely positive and negative as possible. Cuy would write the electronic formula of pentane as follows:

$$\begin{array}{ccccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | & | \\ \text{H}-\text{C}- & + & \text{C}+ & - & \text{C}- & + & \text{C}+ & - & \text{C}- & \text{H} \\ | & | & | & | & | \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$$
 and that of propylene bromide as follows: $\text{H}-\text{C}=\text{C}^+-\text{C}^--\text{Br}$

From Cuy's theory it would be logical to expect HBr to add on to this molecule with the negative bromine on the carbon atom that was positive and the following compound be obtained:

$$\begin{array}{ccccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | & | \\ \text{H}-\text{C}- & \text{C}- & \text{C}^+-\text{Br} & & \\ | & | & | \\ \text{H} & \text{H} & \text{H} \end{array}$$
 but such is not the case, the following compound being obtained:

²³

J. Am. Chem. Soc. 42, 503, (1920).

²⁴

J. Am. Chem. Soc. 46, 247, (1924); 47, 1459, (1925).

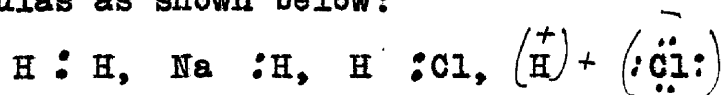
theory is untenable and that much of the evidence advanced in favor of it is not valid. Lucas points out that it is possible to explain all the reactions that Cuy explains by his theory by the theory of electron displacement which was advanced by Lewis.

IV. Lewis' Theory of Electron Displacement

25

In 1916 G. N. Lewis published a paper in which he represented the valence bond between the atoms of a molecule by means of a pair of dots .. which he uses to represent electrons, and said that the position of this pair of electrons in relation to the two combined atoms determined its polarity.

Lewis states this in the following words: "The pair of electrons which constitutes the bond may lie between two atomic centers in such a position that there is no electric polarization, or it may be shifted toward one or the other atom in order to give to that atom a negative, and consequently to the other atom a positive charge. But we can no longer speak of any atom as having an integral number of unit charges except in the case where one atom takes exclusive possession of the bonding pairs and forms an ion". Lewis represents these displacements of electrons in formulas as shown below:

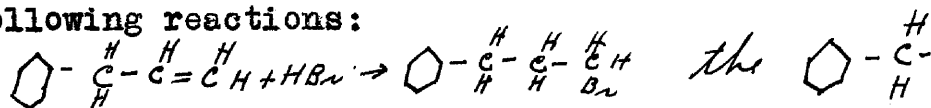


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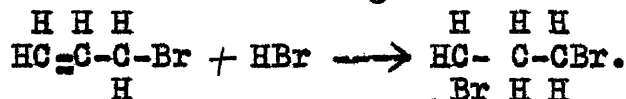
The Atom and the Molecule. J. Am. Chem. Soc. 38, 762, (1916).

Lewis states that ^{the} normal state of a molecule is one in which each atom has a stable group of eight electrons except hydrogen which has two. In the case of double bonds Lewis says that each atom shares two pairs of electrons instead of one pair as in the case of the single bond. He writes the structure of ethylene as follows: $H:\overset{H}{\underset{H}{C}}::\overset{H}{\underset{H}{C}}:H$. Lewis says that a negative element or radical is one which tends to draw toward itself the electron pairs which constitute the outer shells of all neighboring atoms and that an electropositive group is one that attracts to a less extent, or repels, these electrons.

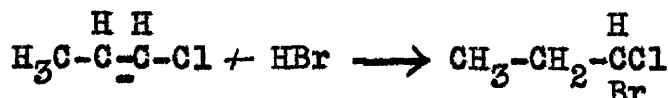
Thus in the addition of halogen acids to compounds containing double bonds the halogen would hook on to the end of the double bond farthestest from the most negative end of the molecule as in the case of the following reactions:



is more negative than the hydrogen.



The bromine is more negative than the hydrogen. But Lewis' idea seems not to hold for all cases as shown below.

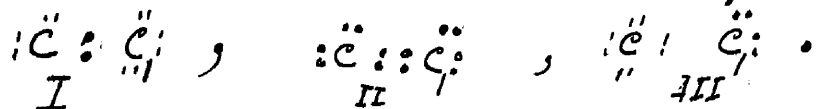


Here the chlorine is considered by Lewis to be a more negative group than CH_3 but the bromine added on the

carbon atom nearest the chlorine instead of the one most distant.

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{HC} = \text{CBr} + \text{HBr} \longrightarrow \begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{HC}-\text{CBr} \\ | \quad | \\ \text{H} \quad \text{Br} \end{array} \end{array}$$
 This gives a similar result to the reaction above. These reactions show the weakness of the Lewis theory as a means of predicting substitution at the double bond.

²⁶
 Carothers in a paper published in 1924 adds to Lewis' theory by stating that one pair of electrons may be held in common by both or may exist first in one atomic shell and then in the other, thus giving the double bond three forms in equilibrium with each other, one inactive form and two active forms, thus:



Forms I and III are active and II is inactive.

He states that the active forms exist only momentarily and the extent of dissociation is dependent upon the effective nuclear charges of C and C₁ (the atom having the higher effective nuclear charge retaining the extra electron), the medium, temperature, pressure and concentration. Attached groups influence the effective nuclear charge of an atom in proportion to their effective nuclear charge.

V. Theory of Partial Polarity

In a paper entitled "The Electronic Conception of

Valence and Heats of Combustion of Organic Compounds"
by M. S. Kharasch and B. Sher²⁷, a newer conception
of the valence bond is discussed. They improve upon
the Lewis theory in their treatment of the double bond.
In their treatment of the double bond they assume,
basing their assumptions on the theory of Bohr and
upon experimental facts, that one pair of electrons is
always shared equally by the two carbon atoms, as in
saturated hydrocarbons. The second pair may be shared
by both to the same extent in one class of unsaturated
compounds but in the other class this second pair of
electrons may be displaced from the valence shell to
different energy levels, depending upon the force
exerted by the groups attached to the doubly linked
carbon atoms.

They reason as follows: Since the final product
of combustion of any organic compound is carbon dioxide,
it is logical to assume that in a system such as methane,
methyl alcohol, formaldehyde, formic acid, carbon
dioxide, the arrangement of the eight electrons in
methane be the first reference position and that of
carbon dioxide the other reference position and that
all the other forms could be referred to as occupying
positions intermediately between those stages.

Furthermore, it is assumed that the displacement of

²⁷

J. Phys. Chem. 29, 625, (1925).

electrons from the methane arrangement to that of carbon dioxide occurs in stages.

Theoretically these energy levels may have any value, but from the heats of combustion of unsaturated compounds these levels exist in definite steps. To illustrate, 13 Kg. cal. of energy are required to move an electron from the valence shell to the first energy level, 6.5 Kg. cal. to move it from the first energy level to the second, etc.

These energy levels may be represented as shown below in Figure I.

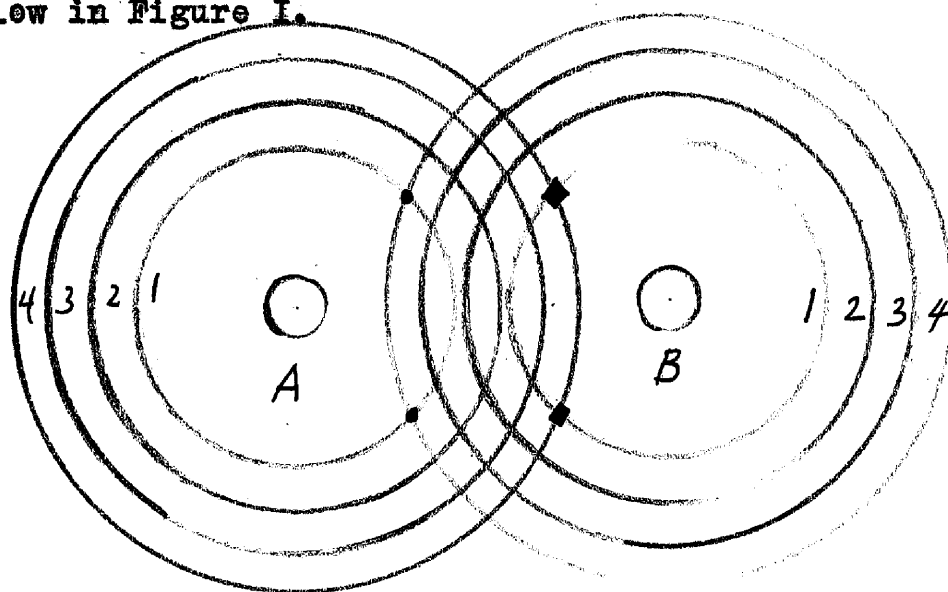


Figure I.

Circles 1,2,3 and 4 representing different energy levels. Now, if A and B represent doubly linked carbon atoms, and if a slightly more negative group is attached to A than to B the pair of electrons may be moved out from A in the direction of B so that they lie in energy level

1 of A and 4 of B, as show by the round dots. If the group linked to A is very strongly negative the pair may be displaced in the direction of B until they rest in level 4 of A and 1 of B as shown by the squares.

The energy levels occupied by this pair of electrons as seen above depends upon the electronegativity of the groups attached to the carbon atoms the double bond occurs between. A series of the relative electronegativity of many of the more common groups have been determined by Kharasch and Marker²⁸ and by Kharasch and Flenner²⁹. These results are given in Table I.

Types of Double Bonds between C-C Atoms from the Standpoint of the Theory of Partial Polarity

As far as the energy of the molecules is concerned, we have to consider the following possibilities as types of double bonds:

1. A :
2. A : B
3. A : B
4. A : B
5. A : B

A simple assumption but one which is borne out by agreement between calculated and experimentally deter-

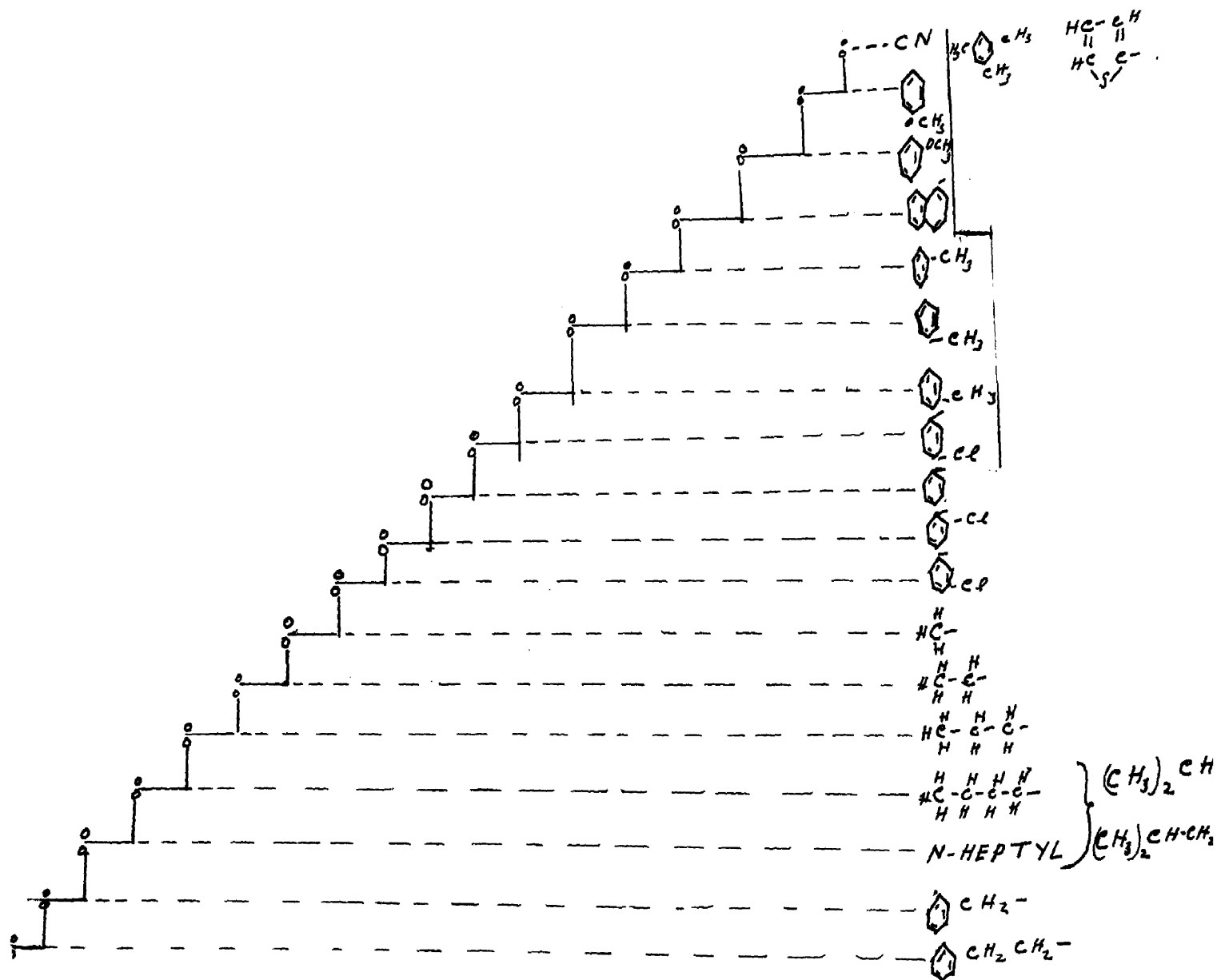
²⁸

J. Am. Chem. Soc. 48, 3130, (1926).

²⁹

Doctor's Thesis Presented by A. L. Flenner (1927).

Order of Electronegativity of Organic Radicals



mined values, is that the pair of electrons held together by two carbon atoms in saturated aliphatic hydrocarbons may be considered midway between their respective valence orbits and the orbit which the electrons occupy in carbon dioxide. The total energy which they supply upon combustion is thus the same as if we had a pair of electrons held in the normal valence orbit of one carbon atom. Types 1, 2 and 3 may be considered to belong in that category. The excellent agreement of the calculated heats of combustion of some eighteen saturated hydrocarbons³⁰ with experimentally determined values, an agreement well within the limits of experimental error, indicates the plausibility and at least the approximate correctness of the hypothesis. It is fully appreciated that this is merely a rough approximation of the truth, but until more refined experimental methods of attack are available the hypothesis covers the ground adequately.

However, this attack of the problem suggests immediately that in the case of sharing of electrons as represented in 4, the molecule contains a larger amount of energy, namely that necessary to pull the electrons out from the normal valence orbit of atoms A and B into the outer orbits, that upon combustion this molecule should furnish a larger amount of heat

³⁰

Kharasch and Sher. J. Phys. Chem. 29, 630, (1925).

than calculated upon the assumption applicable to types 1, 2 and 3. Unfortunately the data at hand do not allow the drawing of far-reaching conclusions.

³¹
Schmidlin determined the heat of combustion of a molecule which would be predicted to have a bond similar to 4 between two carbon atoms, namely hexaphenyl ethane. Calculations from the formula of Kharasch and Sher, assuming the carbon to carbon bond to be similar to 1, 2, and 3, give 2370.4 Kg. cal. for the heat of combustion while Schmidlin obtained 2381 Kg. cal. The difference between these two values, namely 10.6 Kg. cal., could be ascribed to potential energy accumulated in the molecule, when the valence electron was moved out from the normal valence shell into a position corresponding to bond 4. However, it is also noticeable that the difference amounts to only 0.5 per cent, which could be ascribed as being within the limits of experimental error of Schmidlin's determinations. But in their paper Kharasch and Sher ³² give a table of six hydrocarbons where they add 13 Kg. Cals. per mol to obtain the experimentally determined values.

³¹
Ann. Chim. Phys. 8, 7-245, (1906).

³²
loc. cit.

TABLE II.

Unsaturated Hydrocarbons

Name	No. of Electrons	Calc.	Observed
Trimethyl ethylene	30	794.5	796.0 Zub.
Hexylene	36	950.8	952.6 Zub.
Camphene	56	1471.8	1469.4 A.R.E.
Methylene cyclohexene	40	1055.0	1052.0 Roth.
Ethylene cyclohexene	46	1211.2	1209.2 Roth
Sylvestren	56	1471.8	1466.5 A.R.E.

The heats of combustion of substituted ethylene derivatives indicate that they contain a pair of electrons displaced from the carbon atoms or atoms. Reference to Figure I. will help to make this clear. For, in these molecules, two carbon atoms share one pair of electrons in the same manner as two carbon atoms of saturated hydrocarbons, but the second pair of electrons is removed from both of the nuclei. Thus, it can be located in shell 3 of atom A and shell 4 of atom B. The molecule will thus have an electric moment in that part of the molecule. Furthermore, since energy is required to move electrons from the normal valence shell of the carbon atom to shells outside the valence

shell, that amount of energy should be considered in the calculation of the ethylene derivatives. The formula for the calculation of ethylene derivatives is therefore $H = 26.05 \times N + A$, where A is the amount of energy necessary to move a pair of electrons from the normal valence shell to the position they occupy in ethylene derivatives. This value of A we find to be a fraction of the constant employed: namely, 13 Kg. Cal. per mol. The equation for ethylene derivatives, therefore, becomes: $H = 26.05 \times N + 13$. The values for six unsaturated hydrocarbons of this type are given in Table II. The agreement between the calculated and experimentally determined values is very good.

The bond corresponding to type 5 is supposedly met with when two strongly electronegative radicals share a pair of valence electrons in common. Due to the great attraction of each one of those radicals for electrons they share these electrons more in inner shells than those which are not so strongly electronegative. The total energy which such molecules furnish upon combustion would, therefore, be smaller, for it would require more energy to displace the electrons into the outermost orbits. The radicals which would begin to exhibit that tendency are all those that appear above the phenyl radical in the table of the electronegativity of organic radicals on page 23.

The above discussion gives a general picture of the theory of partial polarity as applied to the double bond, but Kharasch³³ has written up seven postulates which are in a more useful form. They are as follows:

Postulate 1. There is a definite polarity at the double bond, so that unsaturated derivatives of the ethylene type have a definite electrical polarization in at least one part of the molecule.

Postulate 2. In the case where the radicals attached to the carbon atoms of the double bond are about the same in electronegativity it is possible to produce either form I or III³⁴, in stable form and not unstable as Carothers states.

Postulate 3. The second pair of electrons constituting the double bond is always held in outer orbits by one of the carbon atoms and some closer inner orbit of the other, the particular orbit depending upon the nature of the radicals attached to the double bond.

Postulate 4. The relative position of the second pair of valence electrons of the double bond depends upon the nature of radicals attached to it in such a way that they are always on the opposite carbon atom to that carrying the most electronegative radicals.

Postulate 5. Alkyl and aryl radicals are more

³³

loc. cit.

³⁴

See discussion of Carothers' paper on page 19.

electronegative than the hydrogen atom.

Postulate 6. 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 whole molecule.

Postulate 7. In case the radicals attached to the carbon atoms of the double bond are all different the same principles apply as developed for compounds in which two radicals of the same type were assumed to be attached to a carbon atom.

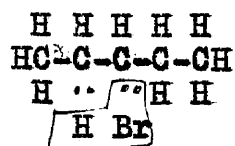
Comparison of the Theory of Partial Polarity with that of Lewis

Thus in the case of the addition of HBr to

$$\begin{array}{ccccccc} & H & H & H & H & & \\ & H & H & H & H & & \\ HC & -C & -C & =C & -CH & & \end{array}$$
 according to the theory of partial polarity of Kharasch one would expect to get most of the bromine adding on in the two position but Lucas³⁵ found that when the above reaction was carried out he obtained 78 per cent of the 3 brom compound and 22 per cent of the 2 brom compound. The work of Lucas was repeated to determine if he was correct. We obtained the same results as Lucas did. But Lucas and ourselves made the pentene by removing HBr from $\begin{array}{ccccccc} & H & H & H & H & & \\ & H & H & Br & H & & \\ HC & -C & -C & -C & -CH & & \end{array}$, when this unsaturation took place thus:

³⁵

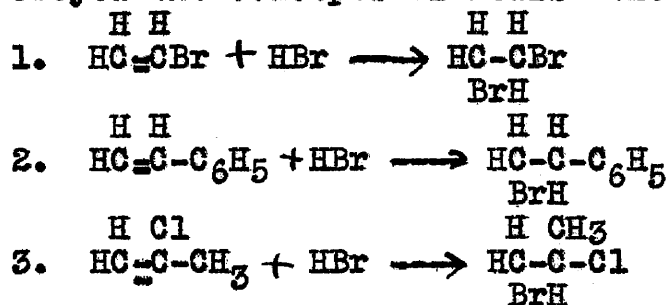
J. Am. Chem. Soc. 47, 1459, (1925).



leaving the extra pair of electrons held by carbon atom 2. Since the difference in electronegativity of the CH_3 and the C_2H_5 is only slight (as shown by the table of electronegativity), the more electronegative CH_3 group will not be able to displace these electrons over to carbon atom 3. Thus when HBr is added on the greater portion will go to form the 3 brom compound again. Kharasch and Starkey³⁶ have shown in their work on vinyl bromide, which was prepared by removing HBr from ethylene dibromide as in the case of the pentene, that when they added HBr to the vinyl bromide as in the case of adding HBr to the pentene they obtained from 99-100 per cent ethylidene bromide. In this case they had a strongly electronegative Br working against a weakly electronegative H. Thus the electrons were pushed over in the direction of the C atom containing the H atom and the Br added on to the carbon atom already containing a ^{bromine} ~~carbon~~ atom. When Lucas used the action of HBr on pentene (prepared as he prepared it) he failed to take into consideration the concept of interdisplacement of the electrons to outer energy levels, therefore his results are not as

conclusive as they might be in respect to proving Lewis' theory and in disproving the theory of partial polarity.

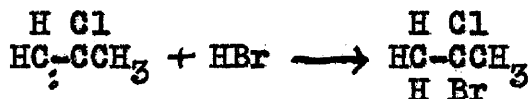
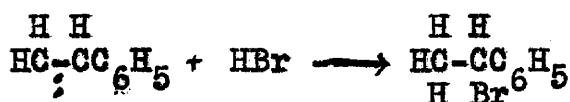
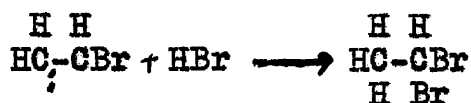
It is surprising that Lucas and his collaborators while extending and defending the Lewis theory have not considered a number of simple reactions which are well known and invalidate the theory they propose. The three examples given here have been mentioned before in this paper but for purposes of comparison they will be listed again. The following three compounds on addition of HBr should give the end products shown if they obeyed the concepts of Lewis' theory:



But in each case this conclusion is in complete disagreement with experimental facts.

If we write down these examples, to which the Lewis theory fails to apply, and apply the above mentioned postulates of Kharasch 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 4, the second pair of valence electrons would be found on the carbon atom opposite the one carrying the most electronegative radical. Thus we would have the following electronic formulas for the three compounds and the addition products would be as shown. These are the products reported in the literature.



Effect of Energy on Double Bonds

After we had proved that Lucas' results in regard to the bromides made from $\begin{array}{c} \text{H H H H H} \\ \text{HC}-\text{C}-\text{C}-\text{C}-\text{CH} \\ | \quad | \quad | \\ \text{H H} \quad \text{H} \end{array}$ were correct we decided to try out experimental work to determine the effect of the application of energy on the position of the electrons at the double bond in the pentene.

The double bond in a compound represents a point of weakness in the molecule and affords a point for rearrangements to take place. These rearrangements are usually brought about or affected by the application of energy in the form of heat or light. Tautomeric shifts are as a rule effected by heat and light, and

geometrical isomers are changed from one form to the other almost universally by energy in the form of heat or light.

The example of maleic and fumaric acids is one of the best known of geometrical isomerisms. Fumaric acid is converted into maleic acid by the means of heat. Derivatives of these two acids also show similar changes by the application of heat. Maleic chloride will pass into fumaric chloride on standing. Paal and Schulze³⁷ have shown that sunlight converts yellow trans dibenzoyl ethylene into the colorless cis form. Probably the most interesting method of effecting geometrical inversion is by the use of light rich in ultra-violet rays, such as is furnished by the mercury vapor lamp.

³⁸Stoermer has published a number of papers dealing with the exposure of stable ethylene compounds to ultra-violet light. He states that the conversion of the laible into the stable modification by the action of light is not uncommon. According to Stoermer the reverse takes place in the coumeric^{acid} series, the stable changing to the laible form under the influence of ultra-violet rays.

A large number of rearrangements brought about by

³⁷

Ber. 35, 168, (1902).

³⁸

Ber. 42, 4865, (1909); 44, 637, (1911); 47, 1786, (1914)

ultra-violet light in organic molecules containing³⁹
double bonds are reviewed by Ellis and Wells .
They say that "hydrocarbons and their simple derivatives
rayed with ultra-violet generally polymerize. Some
of those possessing the more complex configuration
undergo transformation into stereoisomers. Substituents
frequently influence the course of the reaction, and
are sometimes split off, or take part in side reactions.
When oxidizing or reducing agents are present, these
sometimes enter into the reaction".

⁴⁰
Laudau has shown that acetylene and ethylene
are polymerized by the rays from a 500 volt mercury
lamp. These phenomena led us to carry out experi-
mental work on pentene and from the results obtained
we believe that we have definite evidence of the
existence of the electromers of pentene.

Proof of the Existence and Isolation of Electromers of Pentene

The fact that 78 per cent of the 3 brom compound
is obtained when the pentene is treated with HBr is
in agreement with Lewis' theory and in disagreement
with the theory of partial polarity. According to
Lucas the molecule of pentene should have the electronic

³⁹

The Chemical Action of Ultra-Violet Light. Ellis & Wells
⁴⁰
Compt. rend. 155, 403, (1902).

structure given in formula I while according to the theory of partial polarity it should have the electronic structure given in formula II.



I.



II.

However, it is only logical to assume from the theory of partial polarity that if the molecule were shaken up by the application of energy that it would tend to go over into its most stable configuration, according to the partial polarity theory which is configuration II. An indication in that direction was observed in the fact that 22 per cent of structure II existed, and it was assumed that it was formed during the time when the 2 pentene was heated. From that the conclusion was evident that in order to transform the 2 pentene of structure I into structure II, it would be necessary to apply energy to it. This was done by means of heat and ultra-violet light. A quantity of pentene was divided into two parts. To the first part HBr was added at once and it gave the mixture of 22 per cent of 2 brom and 78 per cent of 3 brom compound. While the second half was heated for 16 hours at 100° C, at the end of which time the bromide was made as described in the experimental part. This time, however, as shown in Table IV the products

were a mixture of 32 per cent of the 2 brom compound and 68 per cent of the 3 brom compound. The addition of HBr, therefore, indicates, that after heating for 16 hours, 32 per cent of the 2 pentene of structure II and 68 per cent of 2 pentene of structure I. By carrying out an analogous experiment by subjecting the pentene to ultra-violet light for 16 hours and making the bromides as given in the experimental part, a mixture of 42 per cent of 2 brom pentane and 58 per cent of 3 brom pentane were obtained. The addition of HBr, therefore, indicates that after radiating for 16 hours a mixture of 42 per cent of 2 pentene of structure II and 58 per cent of 2 pentene of structure I was obtained.* It is proposed to call these structures electroisomers and we believe that this is the first observed and proved experimental case of electroisomers (with the exception of the preliminary work carried out by Starkey under the direction of M. S. Kharasch). We are also of the conclusion that in the preparation of 2 pentene by the method of Lucas and Moyse we have a mixture of 78 per cent of pentene of structure I and 22 per cent of structure II, and that by subjecting to energy the pair of valence electrons are shifted so as to produce 42 per cent of structure II and 58 per cent of structure I. From this we are inclined to interpret addition reactions where two products are

*See page 36a.

For sometime now it has been a recognized fact that certain substances such as codliver oil have been very efficient in correcting diets deficient in vitamin D. It is also thought that vitamin action is closely related to unsaturation as far as structure is concerned. Experiment has shown that codliver oil contains certain unsaturated compounds, also that codliver oil that has been radiated with ultra-violet light has shown a greater activity in correcting vitamin deficiency than that not exposed to ultra-violet radiation. It has been a mystery as to what the possible action of the ultra-violet light has been in effecting this change in codliver oil. I believe that this is the first case in which any work has been done from which a lead may be obtained which would lead toward a theoretical explanation of what causes the greater activity in radiated codliver oil.

formed in the addition of a reagent to a double bond, as arising from the existence of two distinct electromers.

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 conclusion. 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 for that reason work will be done on the oxidation of these electromers with permanganate, a reagent which is less likely to cause shifts from cis to trans forms. However, irrespective of the outcome, the existence of electroisomerism has been definitely established.

General Discussion of the Theory of Partial Polarity of the Double Bond

It is a relatively simple task to predict the absorption reactions at the double bond by making use of the postulates given once the relative electronegativity of the radicals has been definitely established, particularly in cases where the two radicals

are pulling in the same direction. Thus, if in the molecule $R-\overset{\text{H}}{\underset{\cdot}{\text{C}}}-\overset{\text{H}}{\text{C}}-R_1$ 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. However, if both R and R_1 are electronegative then the position of the second pair of valence electrons would depend upon the relative positions of the radicals R and R_1 in the Table of Electronegativity. The valence electrons being closer to the carbon carrying the least electronegative radical. Once this view is adopted it becomes possible to compare the relative electronegativity of such radicals as phenyl and bromine.

The main difficulty of predicting all types of absorption 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 becomes less electronegative than an hydrogen atom.

The first assumption is self evident----it means that such groups as phenyl, methyl, ethyl or naphthyl

are more electronegative than an hydrogen atom. Although it is quite conceivable that an overlapping may occur somewhere. In the second assumption we merely imply that since an electronegative radical attached to a 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.

Thus, while the phenyl radicals and bromine, chlorine atoms or hydroxyl groups or oxygen atoms are individually more electronegative than an hydrogen atom, when they become attached to a methyl carbon atom as in benzyl or bromo methyl or chloro methyl they make those groups less electronegative than hydrogen.

In addition reactions at the double bond, we would expect, therefore, that such groups as benzyl or bromo or chloro methyl 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 we would expect the bromine atom to force the second pair of electrons on the opposite carbon atom. However, in allyl bromide, we would expect that the ^{less} ~~more~~ electronegative bromo methyl group would attract the second

pair of valence electrons of the double bond toward itself.

One word may be mentioned in regard to the electro-negative character of the carboxyl group. Since the carbon atom contains strongly electronegative radicals, oxygen atoms attached to the pair of valence electrons of the carboxyl group (COOH) are held in outer shells and we may consider the whole group as 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.

On the other hand, if the strongly electronegative radical and the carboxyl 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 electroisomerism.

Theoretical Explanation of Ease of Addition of Reagents by Compounds Containing Double Bonds

It is a well known fact that 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 II. For it is at once evident that while we may consider the first step in the absorption reaction of an halogen acid to consist in the addition of the hydrogen ion to the displaced electrons, before the addition is complete, the electrons from halogen must be pulled away from the halogen into the inner shells 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, rather than the bromide and iodide ions. It follows also that the more electronegative the radical 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 hydrogen chloride more readily. Other illustrations are available in the literature. However, it must be remembered at all times that ease of addition implies the valence electrons of that carbon are more readily satisfied in outer layers and with a strongly electro-negative 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.

EXPERIMENTAL PART

Ethyl formate of C. P. quality as obtained from Eastman was dried over phosphorous pentoxide and distilled. Boiling point 54.2° to 54.4° .

Ethyl bromide of technical quality as obtained from Eastman was shaken up well three times with concentrated cold sulfuric acid, then washed once with cool water, thrice with cool sodium carbonate solution, once with cool water and dried over anhydrous sodium sulfate for a day and decanted from the sulfate and distilled. Boiling point 38° .

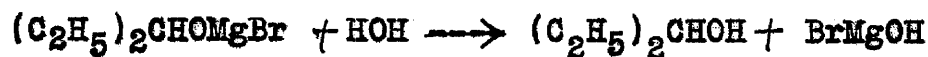
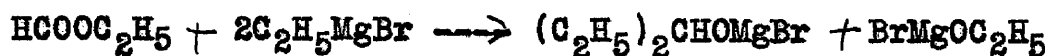
Preparation of Pentanol

The apparatus used was a five liter round bottom flask fitted with a mercury sealed, mechanical stirrer, a reflux condenser and a dropping funnel. In the flask were placed 225 gms. of magnesium turning (more than 8 mols), and about 1500 cc of sodium dried ether.

A small crystal of iodine was added to start the reaction. To this was added four mols or 872 gms. of the purified ethyl bromide. The bromide was added slowly (about three hours being required to add it) with constant stirring, the flask being cooled by a stream of water playing down over it. After the bromide had been added the water surrounding the flask was kept at about 45° for about thirty minutes, to complete the reaction. Then four mols or 296 gms. of the purified ethyl formate was added slowly, with constant stirring, about two and a half hours being required to add it, the flask being cooled by allowing a stream of water to spray over it. The stirring was continued for thirty minutes after the formate had been added. The mixture was then poured slowly on cracked ice acidulated with sulfuric acid (about 2 to 3 per cent). The 3 pentanol was extracted with ether. The ether was removed by distillation, the temperature being increased until no more distillate would come over at a temperature of 80° to 85° . Then the mixture remaining in the distilling flask was washed several times with a cool solution of sodium chloride to remove the ethyl alcohol that had not been removed by distillation. It was then washed once with cool water and dried over anhydrous sodium sulfate and distilled, all coming over below 114° was

subjected to the same treatment as above to remove the last traces of ethyl alcohol and water. On redistillation it boiled over at 114° . The distillates boiling at 114° were combined and fractionally distilled through a Hempel column, the greater portion boiling over at about 115° . Yield about 65 per cent.

Reactions:

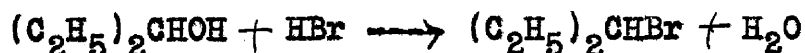


Preparation of 3 Brom Pentane

The carbinol was put in a small round bottom flask and cooled to -10° . It was then saturated with HBr, generated by dropping bromine on a paste of red phosphorous, sand and water. The HBr was passed through two large tubes containing slightly moistened red phosphorous and sand suspended in glass wool, then through a trap containing red phosphorous, after which it passed through two large tubes containing phosphorous pentoxide suspended in glass wool. The flask containing the saturated carbinol was stoppered with a rubber stopper carrying a glass tube to which was fastened a toy rubber balloon to act as an expansion chamber. The flask was placed in a water bath and heated to 60° - 65° and kept at that temperature until the pressure

was reduced. Then the bromide layer was separated and the residue subjected to the same procedure. This was repeated once again but no bromide was obtained. The upper layer in each case was the bromide.

The bromide was washed four times with cool water, twice with ice cold concentrated sulfuric acid, twice with cool water, twice with cool sodium carbonate solution, once with cool water and dried over anhydrous calcium chloride for several hours. It was decanted from the calcium chloride and distilled through a Hempel column. It distilled over between 117.5° and 118.8° , The greater portion coming over at 118.3° . Yield about 85 per cent. It had a refractive index of n_D^{20} 1.4443.



Preparation of 2 Pentene

One mol or 150 gms. of the 3 brom pentane was dropped slowly into a boiling solution of 150 gms. or $2\frac{1}{2}$ mols of KOH in 225 gms. of ethyl alcohol, (95 per cent alcohol) heated on an oil bath 125° to 130° . The vapors were passed through a reflux condenser through which water at 40° was running, which served to condense ethyl alcohol, then through a condenser through which cold water was running, into 125 cc of dry xylene (B. P. 138° - 140°) cooled by an ice and salt mixture. (See Figure II for diagram of apparatus).

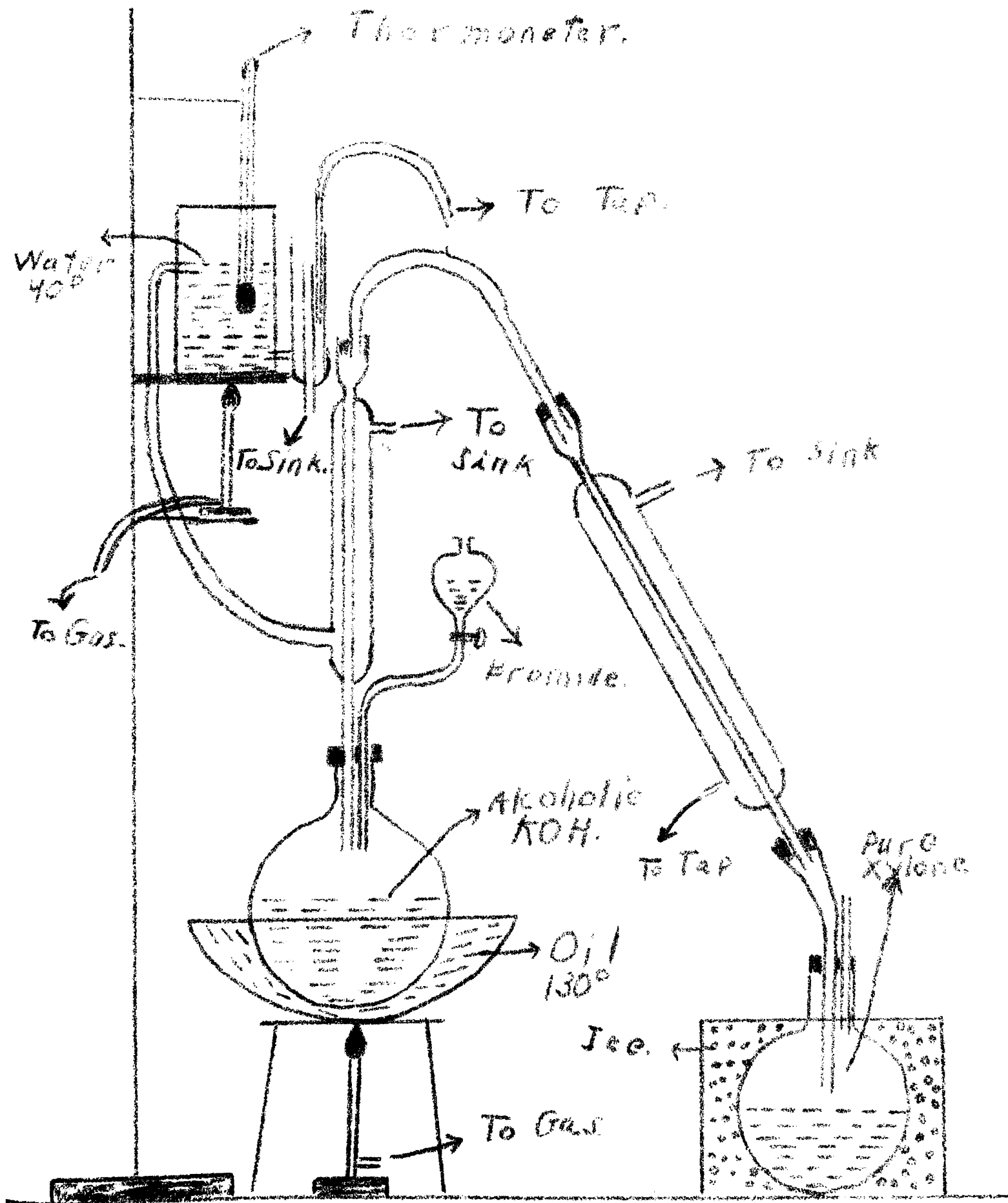
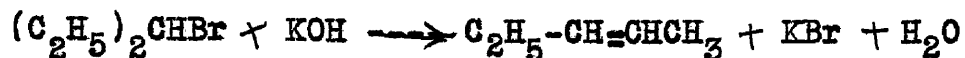


FIGURE II.

The solution of 2 pentene was washed carefully with cold water to remove any alcohol that may have been carried over and dried over anhydrous sodium sulfate. Yield 90 per cent or 64 gms.



About 700 gms. of the pentene was made during the progress of this work, it being made on three different occasions. The work that Lucas carried out was repeated on each of the three quantities of pentene made and his results were checked in each case.

In the work on the first sample the directions of ⁴¹ Lucas as given in his paper were followed in detail. About 20 gms. of the pentene as prepared above was distilled between 35° and 37°, by means of a water bath at 90°, through a Hempel column and condenser into a solution of 43 gms. of HBr in 60 gms. of glacial acetic acid cooled to about -5° by an ice and salt mixture. The reaction mixture was allowed to stand for two hours in ice water, then over night in the ice box at 10°. The following day it was poured into water, the bromide layer separated, washed twice with water, once with sodium carbonate solution, thrice with cold concentrated sulfuric acid, once with water, twice with sodium carbonate solution. Then it was

41

Electron Displacement in Carbon Compounds. J. Am. Chem. Soc. 47, 1459, (1925).

allowed to stand several hours over anhydrous calcium chloride, after which it was decanted into a distilling flask and distilled. B. P. 118° - 119° . The pure bromide was allowed to stand a short time in the presence of a small amount of anhydrous sodium sulfate and then the refractive index was determined at 20° by a Zeiss dipping refractometer. Results are given in Table III.

In the following two determinations the relative amounts of HBr and acetic acid were changed and the compound was dried over sodium sulfate instead of calcium chloride and in one case it was subjected to five washings with sulfuric acid instead of three. But the final result in each case was the same. In another case the pentene was subjected to five distillations before the bromide was made but the final result was not altered. The results are given in Table III.

Then it was decided to subject the pentene to the action of energy by heating it in the presence of the xylene in a sealed tube. Mr. Starkey had carried out some preliminary work on this which led us to believe that we could cause a shift of the electrons by means of heat. We were never able to repeat Mr. Starkey's preliminary work.

TABLE III.

Checks on Lucas' Work						
No.	refrac. index	2 brom compd.	3 brom compd.	Gms. acetic acid	Gms. HBr	% HBr in mixture
1	1.44371	22	78	60	43	71.6
2	1.44371	22	78	90	63	70.0
3	1.44371	22	78	84	80	95.2
*	1.44366	23	77	40	39	97.5

*Pentene subjected to five distillations before bromide was made.

Enough (41 gms.) of the pentene xylene solution to give 15 gms. of pentene were placed in a bomb tube and the tube sealed. The tube was suspended in an iron cylinder open at the top and enough water placed in the cylinder to completely submerge the tube. Then the water was kept at a temperature of boiling for eight hours in some cases and sixteen hours in others. Then the bromide was made and purified as given above and the refractive index determined at 20°. The results are given in Table IV.

The results in Table IV show that there was a definite shift of the electrons in the direction of the 2 carbon atom under the influence of heat. It also shows that the same results are obtained by eight hours heating as are obtained by sixteen hours. This would tend to show that probably an equilibrium is established between the two forms.

TABLE IV.

Pentene Heated to 100° C.

: :No.	:Inst. :reading	:Refrac.: :index	: % :2 brom	: % :3 brom	: :Time in
:	:	:	:compd.:	:compd.:	: 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

Further experiments were carried out to determine the effect of changes in temperature and to see if the presence of daylight would have any appreciable effect.

For this purpose a glycerine bath was set up to be used instead of a water bath. The container being a large pyrex tube sealed at one end. As in the previous case the 41 gms. of xylene were sealed in the bomb tube and the tube submerged below the surface of the glycerine. In one case 15 gms. of pure pentene free from xylene were placed in the tube and subjected to the same treatment. In one case bromine was added to the pentene xylene before it was subjected to heat. The bromide was made and purified in each case as before and the refractive index determined at 20°. The results are given in Table V.

TABLE V.

Pentene subjected to Various Temperatures in Presence of Light

No.	Inst. : reading	Refrac. : index	% : 2 brom :compd.	% : 3 brom :compd.	Time : heated : hours	Temp. : Temp.	Solvent : Solvent	added : substance
1	80.2	1.4437	22	78	8	50-60°	xylene	:
2	79.3	1.44351	29	71	14.5	145- 169°	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	:

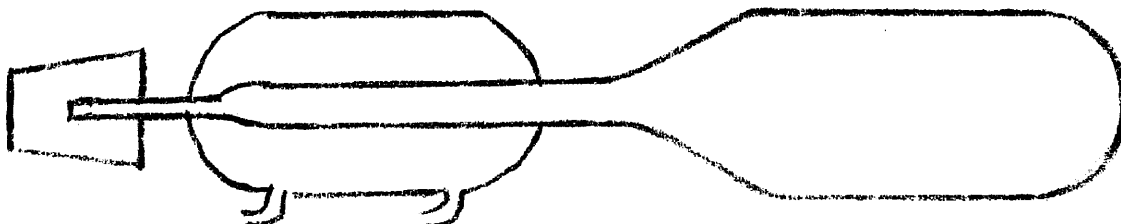
The results in Table V show that there is no shift of electrons caused by a temperature below 50°. Furthermore, they indicate that the optimum temperature for the greatest shift is 100°. In the case where a temperature of 150° was used the shift is not as great as it was in the case of a temperature of 100°. This again would seem to indicate that there is a possibility of an equilibrium being reached. It is seen that the presence of the solvent, xylene, and the presence of small amounts of bromine seem to have no appreciable effect upon the shift of the electrons. Also it is seen that in the case where the temperature was 100° the results checked those carried out in the dark. This shows that the light which is transmitted by glass and a layer of glycerine about three-fourths of an inch in thickness has no effect in shifting the electrons. These results show that the heat is the agent that has caused the shift in the position of the electrons at the double bond in the molecule of pentene as obtained by removing HBr from the 3 brom pentane by means of alcoholic KOH.

After having established the fact that heat would cause a shift in the position of the electrons it was thought advisable to determine if other forms of energy would cause a similar shift. For this purpose we made use of ultra-violet light. The source

of ultra-violet light was a quartz mercury vapor lamp with mercury and tungsten electrodes. The lamp had been used between 1100 and 1200 hours and emitted light from 2,400 to 14,000 $\text{\AA}$. This lamp belonged to the laboratory of Dr. W. W. Coblentz of the Bureau of Standards and it was used by us in Dr. Coblentz' laboratory.

The samples of pentene to be exposed to the ultra-violet light were prepared as follows: The pentene was removed from the xylene by distilling through a Hempel column by means of a water bath at a temperature of 90° - 100° . The liquid coming over having a boiling range of 35° - 38° . This liquid was refractionated by distilling through a Hempel column, the part coming over at 36.5° being used to expose to the ultra-violet. This was placed in a clear quartz tube that had a pyrex condenser fastened to it by means of a graded glass quartz seal. The tube was obtained from Dr. Molar of the Bureau of Standards. See Figure III.

FIGURE III.



The tube was restricted near the end and was closed during the time it was in use by using a rubber stopper that had a hole bored only part of the way through it, and this was stripped over the end of the tube. During exposure the tube was placed within 20 cms. of the source of light and the temperature ranged from 40° - 45° . (The lamp was closed in a metallic case which caused the temperature to remain as high as 45°). A stream of cold water, temperature 5° - 8° , was allowed to circulate through the condenser while it was exposed to the light. Thus the pentene was kept condensed in the quartz tube in the liquid state and did not partially vaporize thus eliminating the factor of pressure during exposure to the ultra-violet.

Experiments were carried out ranging from 6 to 29 hours exposure and the bromides were made and purified as given before. The results of these experiments are given in Table VI.

The results in Table VI show that ultra-violet light effects a shift in the position of the electrons at the double bond in the pentene. We believe that the results given in Table VI are correct but due to the lack of time some of these results were not checked. These will be checked at a later date before they are written up for publication.

TABLE VI.

Pentene Subjected to Ultra-Violet Light

No.	Inst.	Refrac.	%	%	Time	Length of time after
	: reading	: index	: 2 brom	: 3 brom	: hours	: exposure until bromide
			: compd.	: compd.	: exposed:	: was made.
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	: 1.443178	42	: 58	: 16	: Two to four hours
5	: 77.4	: 1.442982	49	: 51	: 29	: Two to four hours
6	: 78.4	: 1.44323:	40	: 60	: 29	: Three days
7	: 78.5	: 1.44327:	38	: 62	: 29	: Two days

It is readily seen from the table that the longer the samples of pentene were exposed to ultra-violet light the greater the shift of the electrons. This would show that the extent of the shift depended directly upon the amount of energy added. This is shown graphically in Figure IV, where the change in refractive index is plotted against time of exposure in hours.

One peculiarity is noticed in the results. That is in the case where the pentene was exposed to the ultra-violet for 29 hours; thus where the bromide was made immediately, 49 per cent of the 2 brom compound was formed. But on allowing the pentene to stand for three days only 40 per cent of the 2 brom compound was formed. If these determinations both represent true results, and we have no reason to believe that they do not, then the electrons will tend to shift back in the direction of the 3 position after the removal of the source of energy. It is to be regretted that we did not anticipate such a condition earlier in the course of the work. If such had been the case we could have kept better account of the time elapsing between the subjecting of the pentene to a source of energy and the preparation of the bromides. In later work this factor will be studied. It is noticed that almost as great a conversion is obtained in 8 hours as in 16 hours and that after 8 hours exposure the conversion is much slower

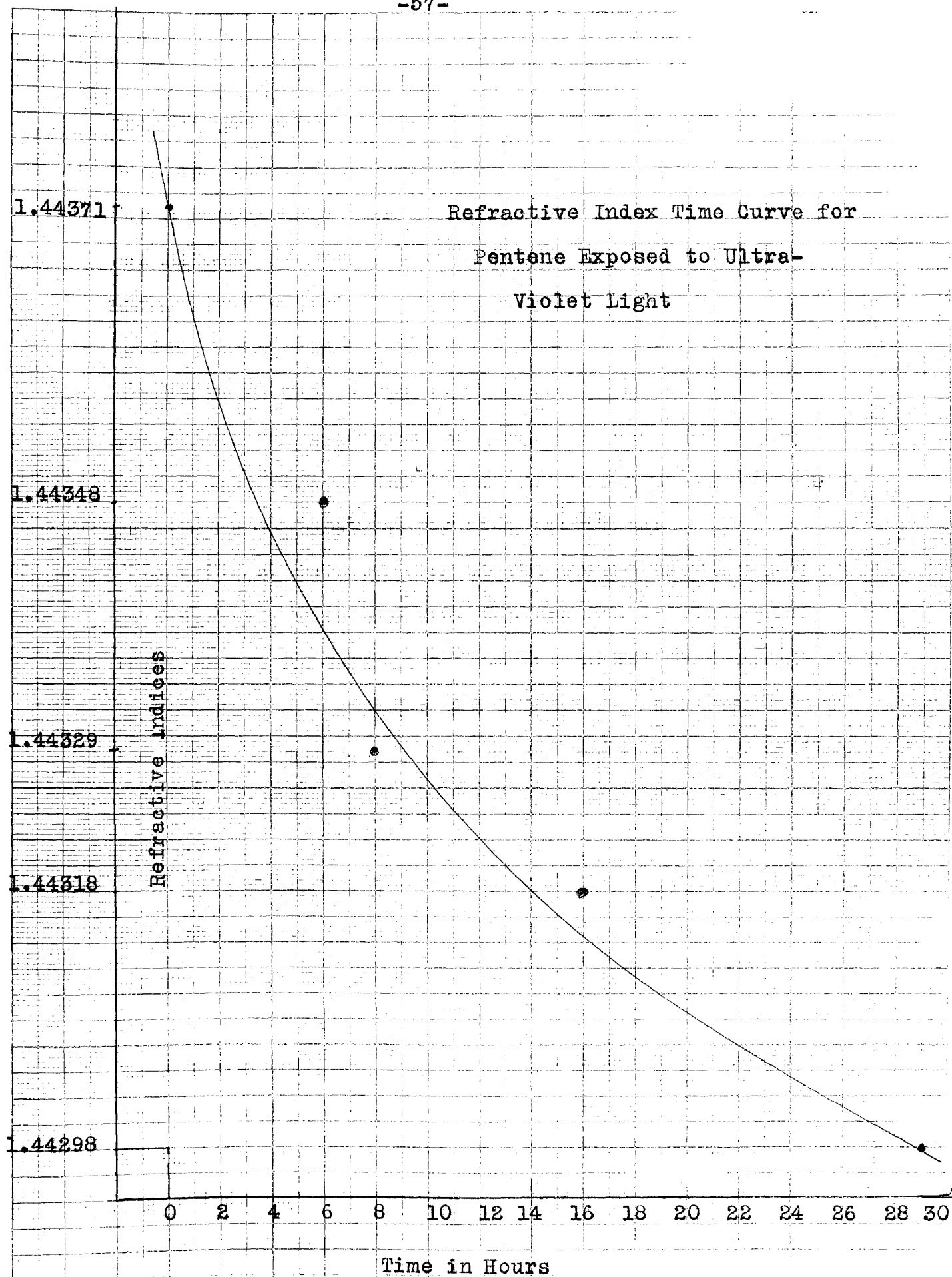


FIGURE IV.

than it was for the first 8 hours. It is also noticed that the conversion for 6 hours is only one half of that for 8 hours. But then the pentene exposed for 6 hours was allowed to stand two days before the bromide was made. Thus allowing for the possibility of the electrons to drop back toward the carbon atom in the 3 position. According to the theory of partial polarity we would not expect the electrons to drop back from the 2 position in the direction of the 3 position. At the present time we have no explanation for this phenomena.

While we were working at the Bureau of Standards in connection with exposing the pentene to ultra-violet light Dr. B. H. Carroll of the Bureau was kind enough to determine and examine the absorption spectrum before and after exposure to ultra violet radiation for varying lengths of time. His report to Dr. Kharasch is as follows:

"The material said to be B-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 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 quartz 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.

TABLE VII.

Time of exposure hours	:Longest wave: length completely absorbed	:Shortest wave: length transmitted	:Longest wave: length at which absorption can be detected
0	: 2753 A ⁰	: 2804 A ⁰	: 3028 A ⁰
8	: 2753 "	: 2804 "	: 3139 "
16	: 2857 "	: 2894 "	: 3663 "
29	: 2926 "	: 2968 "	: 3663

"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 LeChatelier's principle, an equilibrium should be shifted in the direction of decreasing absorption when the shift is due to absorption of radiant energy."

The first two samples of pentene were exposed to ultra-violet light for 8 hours each, and the refractive index was determined before and after exposure to the ultra-violet radiation. These refractive indices were taken by Mr. L. W. Tilton in his laboratory at the Bureau of Standards. These were determined at a temperature of 25⁰, on a new model Palmer Abbe type refractometer reading, by estimation of tenths, to the fifth decimal place. The following results were obtained.

TABLE VIII.

Refractive Indices of Pentene Radiated by Ultra-Violet					
Sample I			Sample II		
:Index before:	:Index	:Avg.:	:Index	:Index	:Avg.:
:radiating	:after	:diff.:	:before	:after	:diff.:
:	:radiating	:	:radiating:	:radiating:	:
:1.37642	:1.37651	.00017:	:1.37577	:1.37597	:.00016:
:1.37642	:1.37662	:	:1.37584	:1.37598	:
:	:	:	:	:	:
:	:	:	:	:	:

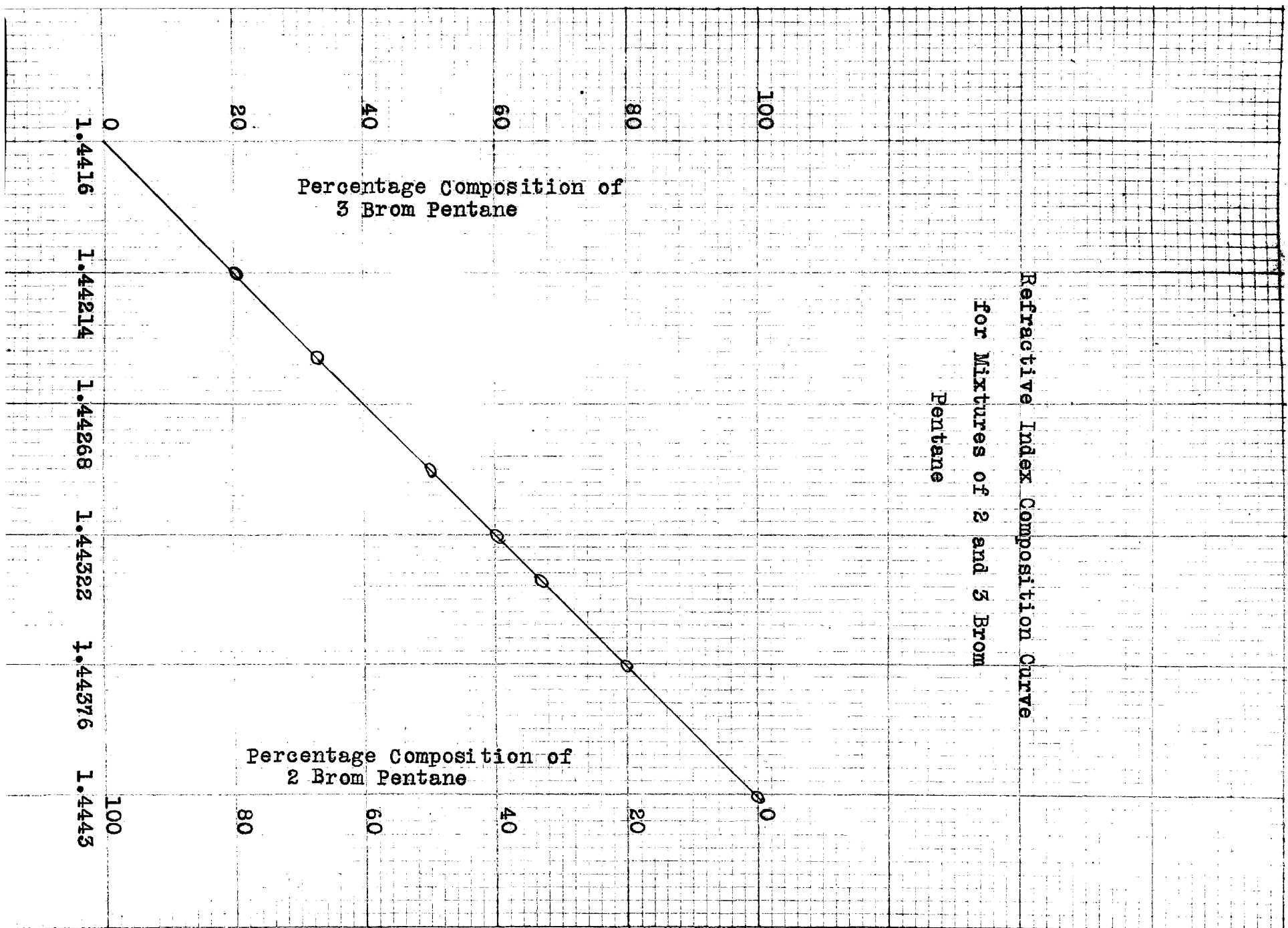
By consulting the table above it is seen that the two samples of pentene did not have the same refractive index to begin with probably due to a small amount of xylene being present. But then it will be seen that the change in index in each case was of about the same magnitude. However, it is considered that this small change in the refractive index does not signify any appreciable change in the composition of the pentene.

The refractive index curve of mixtures of 2 and 3

pentane, which was used in determining the percentage of the 2 and 3 brom compounds from the refractive index, was prepared by Mr. Starkey⁴². This curve is reproduced on page 62. The refractometer used was loaned by the Pharmacy School of the University of Maryland. We believe the experimental error in our results to be less than 3 per cent in the composition of the bromides.

⁴²

Doctor's Thesis Presented by Starkey in June (1926).



SUMMARY

1. It has been demonstrated that energy in the form of heat and light will cause a rearrangement in the position of the valence electrons at the ethylene linkage of 2 pentene.

2. Evidence is given that allows the claim for the existence of two electromers of 2 pentene.

3. The theory of electroisomerism is supported and upheld by the results obtained.

4. The Theory of Partial Polarity incorporated in seven postulates is advanced to explain addition reactions of unsaturated compounds.

5. Evidence is submitted which shows that the Theory of Partial Polarity will serve better to explain addition reactions at the double bond than any other theory available at the present time.