

A TEST OF THE THEORY OF PARTIAL POLARITY. THE ADDITION  
OF HALOGEN ACIDS TO DOUBLE BONDS IN INERT SOLVENTS

By

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A TEST OF THE THEORY OF PARTIAL POLARITY, THE ADDITION OF  
HALOGEN ACIDS TO DOUBLE BONDS IN INERT SOLVENTS

Quite a diversified opinion exists concerning the mechanism of a reaction of a double bond as found<sup>1</sup> in ethylene and its derivatives. In 1869 Markownikow stated that when a halogen acid is added to a double bond the halogen adds to the carbon atom containing the least number of hydrogen atoms. This rule of Markownikow is based upon the fact that propylene adds on HBr to form iso-propyl iodide.

However, it was shown by later investigation that this rule does not adequately represent the addition reaction to all types of substituted ethylene derivatives.<sup>2</sup> Thus, Ipatiew showed that the halogen atom does not always add to the carbon atom poorest in hydrogen atoms. He found that when iso-butylene was treated with HBr over 16% of the primary iso-butyl bromide was formed. Also, when  $\text{CH}_3.\text{CH} : \text{C}(\text{CH}_3).\text{COOH}$  reacts with HI according to the principle of Markownikow the compound formed should be  $\text{CH}_3.\text{CH}_2.\text{CI}(\text{CH}_3).\text{COOH}$ , but instead the compound  $\text{CH}_3.\text{CHI}.\text{CH}(\text{CH}_3).\text{COOH}$  is formed.

Ipatiew believes that the position taken by the halogen was not only determined by the nature of the carbon to which it combined but also by the nature of the radicals linked to the ethylene group, the halogen acid used, the nature of the solvent, and the temperature

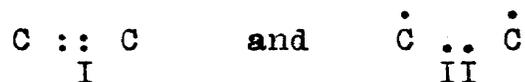
under which the work is carried out. He did not attempt to speculate how these factors influence the addition of the halogen acids.

Michael<sup>4</sup> went a setp further in theorizing as to the action of the double bond. He believed that every atom has a definite quantity of potential chemical energy and that unsaturated or free atoms have a tendency toward greater stability and if no other atoms are available will combine with themselves, part of the energy being used as bonding energy, part given off as heat and part remaining in the atoms as potential chemical energy. He distinguished between positive and negative atoms or units. He considered the carbon atom as nearly neutral or only slightly negative but that it was very susceptible to outside influences imparted by attached atoms or groups. This property he called chemical plasticity.

Thus in the formation of an unsaturated compound such as propylene, some of the potential chemical energy liberated is used up in increasing the mutual saturation. Now in order for addition to take place at a double bond, this mutual saturation bond must be broken and the resistance to reaction is the same in any case and thus the compound formed should be the one having the higher heat of formation. Thus when HBr reacts with propylene the product formed will be  $\text{CH}_3\text{CHBrCH}_3$  since this product permits of the most uniform distribution of free energy in the atoms and therefore should have the higher heat of formation.

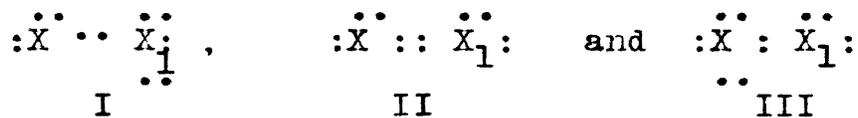
He finds that when HI adds to propylene<sup>5</sup> the ratio of the products are as follows:  $\text{CH}_3\text{CHICH}_3 : \text{CH}_3\text{CH}_2\text{CH}_2\text{I} :: 200-300 : 1$

Lewis in his paper "Valence and Structure of Atoms and Molecules"<sup>6</sup> introduced the electronic conception of the linkage of atoms in a molecule. In his discussion of the double bond he believes that the atoms are held together by two pairs of electrons, which may exist in equilibrium with each other. He represents the two extreme conditions as follows:



I is the inactive form, while II is the active form.

<sup>7</sup> Carothus goes a step farther and states 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:



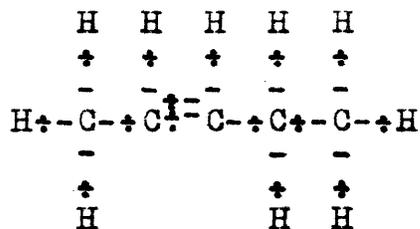
Forms I and III are active, II is inactive. He further states that the active forms exist only momentarily and the extent of dissociation is dependent upon the effective nuclear charges of X and X<sub>1</sub>, (the atom having the higher effective nuclear charge retaining the extra electron) the medium, temperature, pressure and concentration. Attached groups enhance the effective nuclear charge of an atom in proportion to their effective

nuclear charge.

Lowry concludes that the double bond is polar in nature and consists of a covalence which does not break in a chemical reaction, and an electrovalence which does



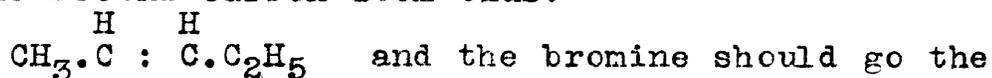
break. For ethylene he writes HC CH. There is another conception of a double bond known as the theory of alternating polarity. According to this theory any ethylene group will contain a positive and a negative carbon; which is positive and which is negative will depend upon the position of the carbons in the chain. For instance, two pentene would be represented thus:



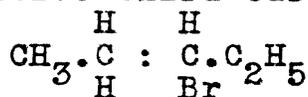
This theory is discussed at length by Cuy.<sup>9</sup> He offers as proof the fact that according to this theory each class of chain hydrocarbons should form two homologous series with respect to physical constants, one containing even numbers of carbon atoms, another containing odd numbers. And such series do exist in certain cases, for instance, the mono-carboxylic fatty acids. On the basis of this theory Cuy predicts that 2 pentene when treated with HBr should give the 2 Br pentane since

carbon 2 is positive. Saytzeff<sup>10</sup> reports obtaining 2 Br pentane by this reaction.

However, careful reasoning will show that no logical and consistent prediction in accord with experiment can be made using the fundamental assumptions of either theory. Often, also, the experiments were not well enough conceived and were not a criteria of what the authors intended to prove or disprove. Thus, Gilman and Peterson<sup>11</sup> found that alkyl magnesium halides will not react with a double bond and offer this as proof against an active form of the double bond as proposed by Lewis, Carothers and Lowry. It must be admitted that their proof is insufficient. Ethylene does not react with HCl but does with HI, Br<sub>2</sub>, Cl<sub>2</sub>, ICl etc. According to Lewis' theory HBr should react with 2 pentene to form 3 Br pentane instead of 2 Br pentane as predicted by Cuy and reported by Saytzeff.<sup>10</sup> For, since the CH<sub>3</sub> group has a stronger pull for the extra electron than has the C<sub>2</sub>H<sub>5</sub> group as shown by the ionization of organic acids and bases,<sup>12</sup> the extra pair of electrons should be displaced toward the second carbon atom thus:



more positive third carbon atom thus:



Lucas and Moyses<sup>13</sup> have carried out the reaction

very carefully under one set of conditions and find that they obtain 78% of the 3 Br pentane and 22% of the 2 Br pentane in support of the theory of transference of electrons.

When vinyl iodide reacts with HI, ICl and BrCl, according to Lewis' theory we should get  $\text{CH}_2\text{I}-\text{CH}_2\text{I}$ ,  $\text{CH}_2\text{Cl}-\text{CHI}_2$  and  $\text{CH}_2\text{Cl}-\text{CHIBr}$ . According to the theory of alternating polarity we should obtain their isomers. 14  
 Namely  $\text{CH}_3-\text{CHI}_2$ ,  $\text{CH}_2\text{I}-\text{CHICl}$  and  $\text{CH}_2\text{Br}-\text{CHICl}$ . Literature gives the latter group of compounds in support of the theory of alternate polarity.

When styrene -  $\text{C}_6\text{H}_5-\overset{\text{H}}{\text{C}}::\overset{\text{H}}{\text{C}}-\text{H}$  - reacts with HBr according to the theory of alternating polarity the product should be alpha Br phenyl ethane -  $\text{C}_6\text{H}_5-\overset{\text{H}}{\text{C}}:\overset{\text{H}}{\text{C}}-\text{H}$   
 $\text{Br}$   $\text{H}$   
 while the theory of Lewis would predict the beta Br compound -  $\text{C}_6\text{H}_5-\overset{\text{H}}{\text{C}}:\overset{\text{H}}{\text{C}}-\text{H}$  15  
 $\text{H}$   $\text{Br}$   
 Again literature decides in favor of the theory of alternating polarity. This reaction is being carried out in our laboratory now.

With these facts in mind we have endeavored to establish certain points in which there is a diversion of opinions and also to carry out certain reactions under various conditions. Since Saytzeff and Lucas report entirely opposite results for the same reaction, that of 2 pentene with HBr, this was our first problem. We repeated Lucas' work first and checked his results exactly.

Ipatiew,<sup>2</sup> Carothers,<sup>7</sup> and others<sup>16</sup> have predicted

that the nature and extent of dissociation of the double bond and the manner in which it adds on other compounds is influenced by the nature of the solvent or medium in which the reaction takes place. To determine what effect this might have we caused 2 pentene to react in the following solvents, in addition to glacial acetic acid as used by Lucas and in our repeat of his work: 95% acetic acid, water, carbon tetrachloride, petroleum ether and in the absence of a solvent. The results are given below:

Solvent used	Composition	
	% 2Br	% 3Br
100% acetic acid	22	78
Carbon tetrachloride	8	92
Petroleum ether	8	92
95% acetic acid	3	97
Water	3	97
No solvent	2	98

The product was analyzed by means of the refractometer. Since the boiling point of 3 Br pentane is 118 - 118.2 and that of 2 Br pentane is 117.5 - 118.5, they could not be separated by fractional distillation. They do, however, have different indices of refraction. The indices were taken with the Zeiss dipping refractometer using prism No. 4. The temperature was kept at 20° C. plus or minus 0.1 degree. The possible error in reading was equivalent to 2 - 3% in composition.



instead of 78% and 22% for the first case. This may or may not mean a difference, since the possible error in the analysis with the refractometer is 2 - 3%. Anyway, the difference is not significant.

It was thought that possibly the final distillation of the product might cause a rearrangement of the atoms in the molecule, thus convertint the 2 Br pentane into the 3 Br pentane. We repeated the first experiment but omitted the final distillation. No change in composition was noted before and after distillation.

Since anhydrous calcium chloride was used as a drying agent it was thought that possibly some reaction might take place between the calcium chloride and the Brompentane. However, no change in composition was found when anhydrous sodium sulphate was substituted for calcium chloride.

The reaction of propylene with HBr was next studied. According to literature <sup>17</sup> these two compounds do not react. However, we obtained a small yield of bromide. It was thought that possibly the compound from which the unsaturated compound was prepared might have some influence on the product formed. Propylene was selected for this work because propylene can be prepared from both normal and iso-propyl bromide. If 2 Br pentane is used to prepare pentene a mixture of 1 and 2 pentene are obtained. The reaction of propylene and HBr was

carried out using propylene prepared from both bromides. The final product was the same in both cases. It was practically 100% iso-propyl bromide.

We then decided to study the action of a halogen acid on a halogen substituted olefine. Since the reaction of HBr on vinyl bromide apparently has not heretofore been studied, we selected that combination. Glacial acetic acid and water were used as the solvents and it was found necessary to seal the mixture in a tube and allow the temperature to rise above the boiling point of vinyl bromide (B.P.16°) in order to have the addition take place. Under these conditions only about 15% yield was obtained. The product obtained in both cases was practically 100% ethylidene bromide.

Since, according to the theory of alternate polarity, 2 pentene should react to form 2 Br pentane, our work would indicate that the conception is not entirely correct and that Saytzeff did not obtain the 2 Bromide. Considering the various conditions under which our work was carried out it is not probable that the 2 Br pentane would be formed under any condition.

Of the two theories discussed above, that of Lewis is no doubt the superior one. According to Lewis and his followers, where a double bond exists the electrons are either shared equally by both doubly linked carbon

atoms, or one pair may be held entirely by one or the other of the doubly linked carbon atoms.

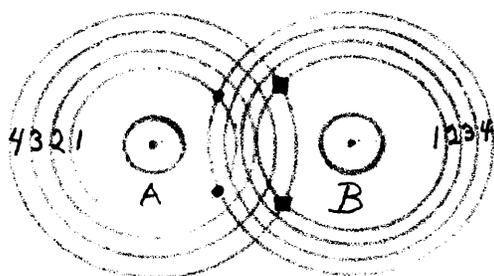
Consequently, according to Lewis' theory in vinyl bromide the presence of the Bromide atom having a greater active nuclear charge than the hydrogen atom, should displace the extra pair of electrons to the carbon atom to which the bromine is attached, thus  $\text{HC} : \overset{\text{H}}{\text{C}} \overset{\text{H}}{\text{Br}}$  and, therefore, when HBr is added on, the positive Hydrogen ion should go to the carbon atom possessing the extra elections thus:  $\overset{\text{H}}{\text{HC}} : \overset{\text{H}}{\text{C}} \text{Br}$ , forming ethylene dibromide, which is not the case. Also in styrene, the more negative phenyl group would displace the electrons in the direction of the alpha carbon atom thus:  $\text{C}_6\text{H}_5 \overset{\text{H}}{\text{C}} : \overset{\text{H}}{\text{CH}}$  and the addition of HBr should produce the Beta bromide thus:  $\overset{\text{H}}{\text{C}_6\text{H}_5} \overset{\text{H}}{\text{C}} : \overset{\text{H}}{\text{CH}} \text{Br}$ . Literature reports the alpha compound as being formed.

In a paper entitled "The Electronic Conception of Valence and Heats of Combustion of Organic Compounds",<sup>18</sup> by M. S. Kharasch and B. Sher, a newer conception of the double bond is discussed. They assume, basing their assumptions on the theory of Bohr and upon experimental facts, that one pair of elections 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 elections 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.

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.

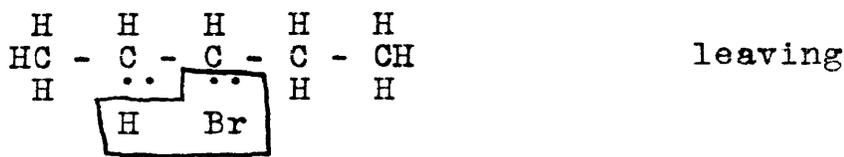
These energy levels may be represented thus:



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 shown by the round dots.

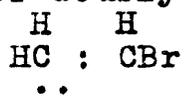
If the group linked to A is very strongly negative the pair may be displaced in the direction of B until they rest in level 4 of A and 1 of B as shown by the squares.

Now, when 2 pentene is prepared from 3 Br pentane by removing HBr the unsaturation takes place thus:



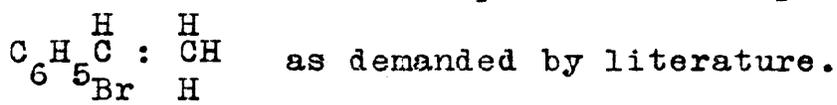
the extra pair of electrons held by carbon atom 2. Since the difference in negativity of the CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> groups is only slight, the more negative CH<sub>3</sub> group will not be able to displace these electrons over to carbon atom 3. Thus when HBr is added on the 3 Br pentane will again be formed.

But, in the case of vinyl bromide we have a strongly electronegative group (Br-) attached to one of the doubly linked carbon atoms. This group would displace the extra pair of electron in the direction of the other doubly linked carbon atom thus:



Thus when HBr adds on to vinyl bromide the hydrogen atom will attach itself to the carbon toward which the pair of electrons were displaced. The bromine will add to the other carbon atom thus forming ethylidene bromide as is the case according to experimental facts, but contrary to predictions made on the assumptions of Lewis' theory.

Further styrene containing the strongly negative phenyl group will have the extra electrons shifted toward the beta carbon atom thus: C<sub>6</sub>H<sub>5</sub> C : CH and the addition of HBr would produce the alpha Br compound thus:



This concept of interdisplacement of the elections

to outer energy levels has not been taken into consideration by Lucas, therefore, his results are not as conclusive as they might be in respect to proving the Lewis theory. They are much more significant in disproving the alternating polarity theory.

#### EXPERIMENTAL WORK

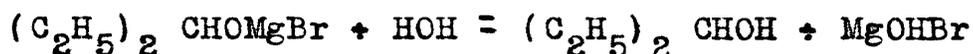
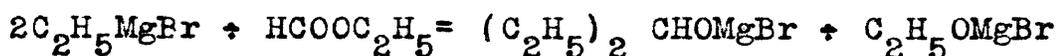
PREPARATION OF ETHYL FORMATE. Four moles of ethyl alcohol and 4.6 moles of concentrated sulphuric acid were mixed with 4 moles of sodium acetate and the mixture left over night. The next day the ester was distilled through a Hempel column. It was then washed with sodium carbonate solution, dried over phosphorus pentoxide and distilled. It distilled between  $54.2^{\circ}$  and  $54.4^{\circ}$  C. The yield was 260 g or 90%.

PURIFICATION OF ETHYL BROMIDE. Ethyl bromide was washed twice with cold concentrated sulphuric acid, then with dil sodium hydroxide solution until neutral, dried over anhydrous calcium chloride and distilled. It boiled at  $38^{\circ}$  C.

PREPARATION OF 3 OH PENTANE. The apparatus used was a 4 liter round bottom flask fitted with a mercury sealed mechanical stirrer, a reflux condenser and a dropping funnel. In the flask was placed 150 g of Magnesium turnings and 2 liters of ether dried over sodium. A small crystal of iodine was added to start the reaction. To this was added drop by drop with constant stirring 654 g

(six moles) of the pure dried ethyl bromide. After this was added and the reaction was complete, 222 grams (3 moles) of ethyl formate was added drop by drop with constant stirring. The mixture was then poured slowly on cracked ice slightly acidulated with sulphuric acid, (about 2%). The 3 pentanol was extracted with ether from which it was separated by fractional distillation. The purified carbinol boiled between  $117.6^{\circ}$  and  $118^{\circ}$  C. Yield 190 g or nearly 75%.

Reactions:



PREPARATION OF 3Br PENTANE. The carbinol was put in a small round bottom flask and cooled to  $-10^{\circ}$  C. It was then saturated with HBr which was generated by dropping bromine on a paste of red phosphorus, sand and water, passed through 2 U-tubes containing slightly moistened red phosphorus and sand, then through a third U-tube containing anhydrous sodium sulphate. The flask containing the saturated carbinol was then stoppered with a cork 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  $60^{\circ}$  C. and kept at that temperature until the pressure was reduced. This was repeated twice but no perceptible change was noted in the volume of the two layers after the second saturation and heating. The top layer which contained the

bromide was washed four times with water, twice with cold concentrated sulphuric acid, twice each with water and sodium carbonate solution, dried over anhydrous calcium chloride and distilled. Boiling point  $118.5^{\circ}$  (Corr.). Yield 285 g or about 90%  $n_D^{20}$  1.4443.

PREPARATION OF 2-PENTENE. Two moles (280 g) of the 3 Br pentane was dropped slowly into a solution of 300 g of potassium hydroxide in 500 c.c. of ethyl alcohol heated in an oil bath to  $125 - 130^{\circ}$ . The vapors were passed through a reflux condenser through which water at  $40^{\circ}$  C. was running, then through a condenser through which cold water was running, into 250 cc. of dry Xylene kept cold by a mixture of ice and salt. The solution of 2-pentene was washed carefully with cold water, then dried over calcium chloride.

A similar quantity of pentene was made three other times as above.

REACTION OF HBr AND 2-PENTENE IN GLACIAL ACETIC ACID.

About 20 g of 2-pentene prepared above was distilled from the Xylene through a hempel column and condenser into a solution of 43 g of HBr in 60 g glacial acetic acid kept cool by a mixture of ice and salt. The mixture stood 2 hours at about  $5^{\circ}$  and then over night at a temperature of  $10-12^{\circ}$ . The reaction mixture was then poured into water and the oily layer separated, washed twice with water, twice with sodium carbonate solution, twice with cold concentrated sulphuric acid, twice with

water, twice with sodium carbonate solution and dried over  $\text{CaCl}_2$  and distilled. The product distilled from 118-118.5° (corr.).

The refractive index of this was run and gave for the D line at 20° C. an index of 1.4437. Since the refractive index of 3-Br pentane is 1.4443 and that of 2-Br pentane is 1.4416<sup>19</sup>, the value obtained indicates a mixture of 22% of the 2-Br pentane and 78% of the 3-Br pentane.

REACTION OF 2 PENTENE AND HBr IN  $\text{CCl}_4$  AND PETROLEUM ETHER AS SOLVENTS. About 20 g of the pentene was distilled from the Xylene and dissolved in 60 g of  $\text{CCl}_4$  kept cold with ice and salt. Since HBr is only slightly soluble in  $\text{CCl}_4$  it was necessary to saturate the mixture of pentene and  $\text{CCl}_4$  in the cold (- 5°) and stopper and allow to react, cool, saturate and stopper again. This was done six times. The mixture was washed twice with water, twice with sodium carbonate solution and the bromide separated from the  $\text{CCl}_4$  by fractional distillation. The constant boiling fraction of bromopentane, (B.P. 118°-118.5°) was washed twice with cold concentrated sulphuric acid, twice with water and twice with sodium carbonate solution, dried and distilled. B.P. 118°- 118.5° (corr.).

This product gave for the D line at 20° C. an index of refraction of 1.4441 which indicated a composition of 8% of the 2 Br pentane and 92% of the 3-Br pentane.

The above experiment was repeated except petroleum ether - B.P.  $36^{\circ}$ -  $37^{\circ}$  was used as a solvent instead of the  $\text{CCl}_4$ . This product was identical in Boiling point and composition ( $n_D^{20}$  1.4441) with the product obtained from the  $\text{CCl}_4$  solvent.

REACTION OF HBr AND 2 PENTENE IN 95% ACETIC ACID. 60 g of 95% acetic acid was saturated with HBr at  $0^{\circ}$  C. and about 20 g of pentene distilled into it. The pentene separated out in a layer above the acid. The mixture was shaken vigorously by a mechanical shaker for three days at room temperature. The mixture was then poured into water and the bromide layer separated and purified as under glacial acetic acid. B. P.  $118^{\circ}$ -  $118.5^{\circ}$  (corr.)  $n_D^{20}$  1.44422 composition 3% of 2 Br pentane, 97% of 3 Br pentane.

REACTION OF HBr AND 2 PENTENE IN WATER. The above experiment was repeated using a saturated aqueous solution of HBr instead of the 95% acetic acid solution. The bromide boiled at  $118^{\circ}$ -  $118.5^{\circ}$  (corr.) and gave for the D line at  $20^{\circ}$  C. a refractive index of 1.44422. Composition 3% of the 2 Br pentane, 97% of 3 Br pentane.

REACTION OF HBr AND 2 PENTENE IN GLACIAL ACETIC ACID AT  $50^{\circ}$  C. The experiment using glacial acetic acid as a solvent was repeated except the mixture was sealed in a hard glass tube and kept at a temperature of  $50^{\circ}$  C. for 12 hours. The bromide was worked up as before. B. P.  $118$ - $118.5^{\circ}$  (corr.)  $n_D^{20}$  1.4438, composition 20% of 2 Br pentane and 80% of 3 Br pentane.

REACTION OF HBr AND 2 PENTENE IN NO SOLVENT. 20 g of dry 2 pentene (B. P.  $35^{\circ}$ -  $37^{\circ}$ ) was saturated with dry HBr gas at a temperature of  $-5^{\circ}$  C., stoppered and allowed to react at room temperature for one hour, cooled, saturated again, etc. five times. The bromide was purified as before. B. P.  $118^{\circ}$ -  $118.5^{\circ}$  (corr.)  $n_D^{20}$  1.44425 composition 2% of 2 Br pentane 98% of 3 Br pentane.

UNDISTILLED BROMIDE. The experiments using glacial acetic acid and water as solvents were repeated but the product after drying was not distilled. No difference in the refractive index was noted.

SODIUM SULPHATE AS DRYING AGENT. The experiment using glacial acetic acid as a solvent was repeated except anhydrous sodium sulphate was used as a drying agent. No difference was observed.

ANALYSIS OF MIXTURES OF 2 AND 3 Br PENTANES. Six mixtures of the 2 and 3 Br pentanes <sup>20</sup> were analyzed by taking their refractive indices to determine if the refractive index is a linear function of the composition. The results are as follows:

Wt. of 2 Br pentane : Wt. of 3 Br pentane : % composition : Observed ref. index : Calculated ref. index

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4	:	0	:	100	:	1.4416	:	1.4416
4	:	1	:	80	:	1.44215	:	1.44214
4	:	2	:	66.6	:	1.44249	:	1.4424
4	:	4	:	50.0	:	1.44296	:	1.44295
4	:	6	:	40.0	:	1.44321	:	1.44322
4	:	8	:	33.3	:	1.44331	:	1.4434
4	:	16	:	20.0	:	1.44378	:	1.44376

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The refractive index is, therefore, a linear function of the composition.

PREPARATION OF n-AND ISO-PROPYL BROMIDES. The n-propyl bromide was prepared in 90% yield from n-propyl alcohol B. P. 97.2°- 97.5° by the sodium bromide method.<sup>21</sup> It was purified in the same way that the 3-Br pentane was purified. B. P. 71.3°- 71.6° (Corr.)<sup>20</sup>  $n_D^{20}$  1.43414.

Iso-propyl bromide was prepared from iso-propyl alcohol (B. P. 82.6°- 83°) in two ways. First, by the sodium bromide method and purified as above B. P. 59.3-60°, yield 90%,  $n_D^{20}$  1.42508. Second, by the method used in preparing 3 Br pentane from 3 OH pentane. Two days were required to complete the reaction. Yield 60% B. P. 59.3°-60°  $n_D^{20}$  1.42508.

#### PREPARATION OF PROPYLENE FROM n- and iso PROPYL BROMIDES.

Propylene was prepared from both n and iso propyl bromides by the method used for the preparation of 2-pentene. The propylene instead of being collected in Xylene, (due to the fact that propylene is a gas ordinary temperatures) was passed through water and then through a drying tube filled with anhydrous  $\text{CaCl}_2$  into a solution of 43 g of HBr in 60 g of glacial acetic acid kept at  $0^\circ \text{C}$ .

#### REACTION OF HBr WITH PROPYLENE IN GLACIAL ACETIC ACID.

The propylene was allowed to pass slowly through glacial acetic acid at  $0^\circ \text{C}$ . for eight hours in both cases. The mixture was then poured into water, the bromide layer separated and purified as in the case of the mixtures of 2 and 3 Br pentanes but was not distilled. The product from the propylene prepared from n-propyl bromide, yield 5 g, gave for the D line at  $20^\circ \text{C}$ . a refractive index of 1.42514 or about 99% iso propyl bromide. The product from the propylene prepared from iso propyl bromide, yield 5 g, gave for the D line at  $20^\circ \text{C}$ . a refractive index of 1.42514 or about 99% of the iso propyl bromide.

#### PREPARATION OF VINYL BROMIDE.

Vinyl bromide was prepared by dropping slowly ethylene dibromide on a 20% solution of KOH in alcohol heated to about  $75^\circ \text{C}$ . The vinyl bromide B. P.  $16^\circ$ - was passed up through a reflux condenser kept at  $18^\circ$  then through a condenser cooled with ice and salt to about  $-10^\circ$ , into cold xylene. The xylene solution was

washed carefully with ice water and dried over anhydrous calcium chloride.

REACTION OF VINYL BROMIDE WITH HBr IN GLACIAL ACETIC ACID.

The vinyl bromide was distilled from the xylene to a solution of 43 g HBr in 60 g of glacial acetic acid kept cold by ice and salt and the mixture sealed in a glass tube and left at room temperature for three days. The product was then worked up in the usual manner and analyzed by means of the refractometer. It was not distilled. Yield about 5 g. This product gave for the D line at 20° C. a refractive index of 1.5129. Since the refractive index of ethylene dibromide is  $n_D^{20}$  1.53789<sup>22</sup> and for ethylidene bromide is  $n_D^{20}$  1.512767<sup>22</sup> the product obtained was over 99% ethylidene bromide.

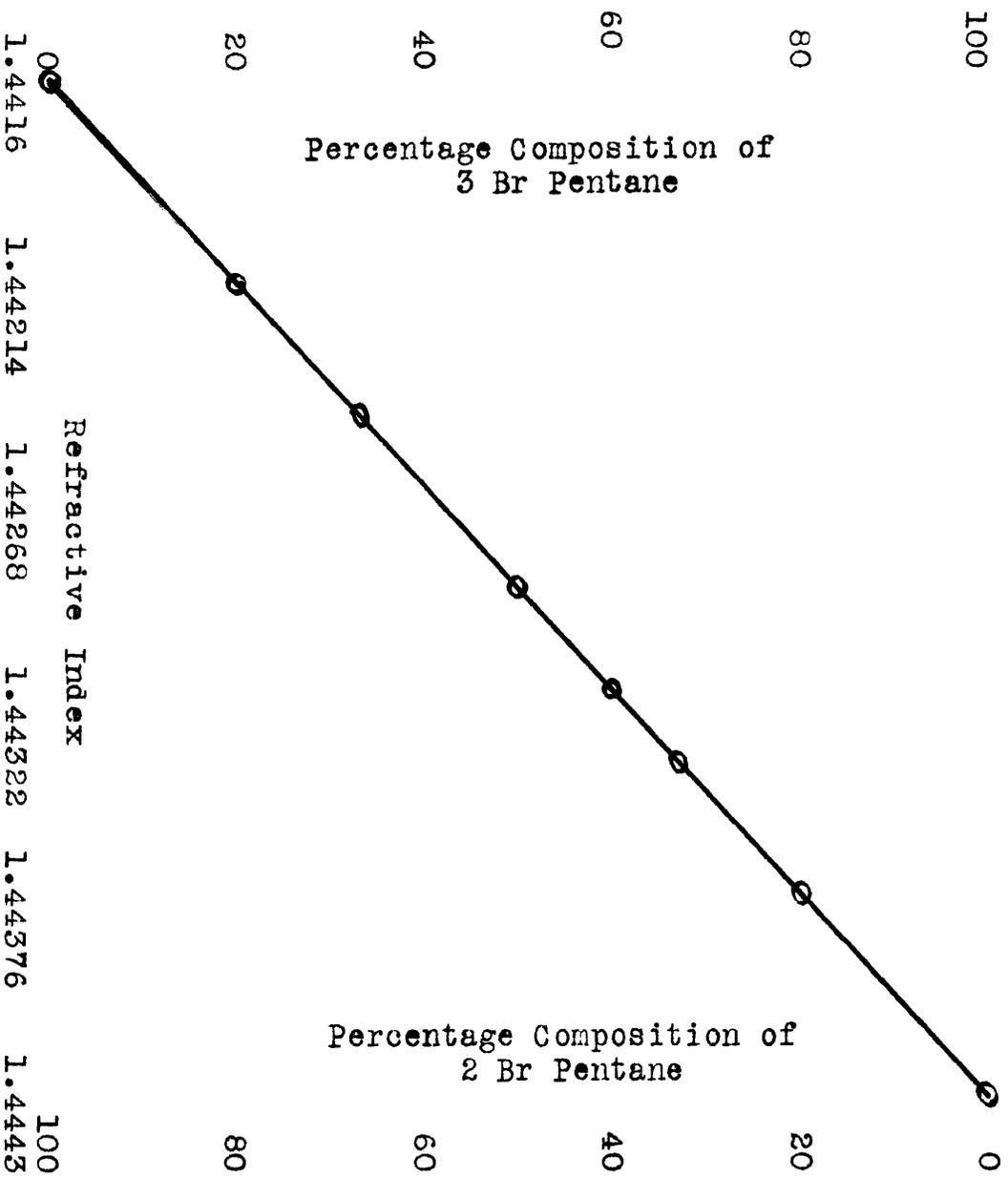
REACTION OF VINYL BROMIDE WITH HBr IN 50% ACETIC ACID.

The above experiment was repeated except the vinyl bromide, 20 g, was added to a saturated solution of HBr in 50% acetic acid. Yield about 3 g  $n_D^{20}$  1.5129, indicating again a product of over 99% ethylidene bromide.

### SUMMARY

1. Markownikow's principle, and the theories of Lewis and of alternating polarity are inadequate.
2. 2 pentene reacts with HBr to form 3Br pentane chiefly and some 2 Br pentane.
3. The nature of the solvent has a small effect on the composition of the product formed in the above reaction.
4. Temperature, distillation and the drying agent have no appreciable effect on the results.
5. The compound from which the unsaturated compound is made does not affect the final product when a halogen acid reacts with an ethylene homologue.
6. Vinyl bromide will react with HBr and the product formed is ethylidene bromide.

R. I. COMPOSITION CURVE FOR MIXTURES  
OF  
2 AND 3 BR PENTANE



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