U.S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP740

Part of Journal of Research of the National Bureau of Standards, Volume 13, November 1934

POLYMERIZATION OF OLEFINS FORMED BY THE ACTION OF SULPHURIC ACID ON METHYLISOPROPYLCARBINOL

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ABSTRACT

The action of 75 percent sulphuric acid on methylisopropylcarbinol at 80° C results in the formation of 2 isomeric decenes, namely, 3,4,5,5-tetramethylhexene-2 and 3,5,5-trimethylheptene-2. The theory proposed by Whitmore for the polymerization of olefins does not explain the formation of the above products without the postulation of a complicated rearrangement. A theory is proposed for the polymerization of olefins, based on the apparent activation of the olefin molecule, causing it to behave as 2 fragments which then add to the double bond of another olefin molecule in the usual manner. This behavior is analogous to the addition of RMgX to a carbonyl group $=C=O$ to yield $=C(R)-OMgX$. From a consideration of the relative calorie strengths of bonds, it is predicted that a C–C bond would be broken more readily than a C–H bond during the addition of the activated olefin molecule to another olefin molecule; thus the products to be expected differ markedly in many cases from those predicted on the basis of a labile hydrogen mechanism. This activation theory for the polymerization of olefins furnishes a simple mechanism for the diisoamylenes studied and for the formation of the known di– and triisobutylenes from isobutylene.

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I. INTRODUCTION

The formation of products of high molecular weight by the action of polymerizing agents on olefins is well known. This reaction has important industrial applications in the manufacture of lubricating oils[1] and synthetic resins.[2] [3]

The extensive literature on the polymerization of ethylene has been reviewed by Stanley [4] and Carothers.[5] Mignonac and Saint-Aunay [6] succeeded in isolating butene-1 and hexene-1 as the first products

[1] Ind. Eng. Chem. 23, 604 (1931).
[2] Ind. Eng. Chem. 24, 1125 (1932).
[3] Carleton, Ellis, Synthetic Resins and Their Plastics, Chemical Catalog Co., Inc., 1923.
[4] J. Soc. Chem. Ind. 49, 349T (1930).
[5] Chem. Rev. 8, 353 (1931).
[6] Bul. soc. chim. 47, 522 (1930).

formed in the action of the silent discharge on ethylene. Pease [7] found butene-1 in the products of thermal polymerization of ethylene and from a study of the kinetics has concluded that this is a chain reaction. Carothers states that in effect at least this reaction involves at the first step the addition of ethylene, as $H+CH=CH_2$, to the double bond of another molecule of ethylene, and then a similar addition to the butylene so formed.

The isomers in diisobutylene prepared by the action of sulphuric acid on tertiary butyl alcohol were found by Whitmore and his students [8] to be 2,4,4-trimethylpentene-1 and -2, in approximately the ratio of 4:1, which confirms the previous work of McCubbin and Adkins.[9]

A mechanism for the polymerization of olefins by acid catalysts has been proposed by Whitmore.[10] He postulates as the first step the addition of a hydrogen ion to the extra electron pair in the double bond to form a positively charged group which then adds to another olefin molecule to form a second positively charged group. This latter group may then liberate a hydrogen ion to form a new olefin molecule. The process is, therefore, catalyzed by any substance which gives hydrogen ions. On the basis of this theory, Whitmore has predicted that the most probable products in the diisoamylenes should be 3,5,5-trimethylheptene-2 and -3, 2,3,4,4-tetramethylhexene-1 and -2, and 2-ethyl-4, 4-dimethylhexene-1.

The purpose of the present work was to determine the structure of the diisoamylenes prepared by the action of sulphuric acid on methylisopropylcarbinol in order to add further to our knowledge of the mechanism of polymerization of simple olefins to complex oils and resins.

II. EXPERIMENTAL

Methylisopropylcarbinol was prepared from isopropyl bromide and acetaldehyde by means of the Grignard reaction as described by Drake and Cooke.[11] The carbinol was treated with one and one-half moles of 75 percent sulphuric acid at 80° C for 20 minutes. This treatment has been shown by Cooke [12] to give the best yield of the unsaturated dipolymer having the empirical formula $C_{10}H_{20}$. The purified decene was fractionated in a 250-cm chain-packed distilling column [13] at the National Bureau of Standards through the courtesy of the late E.W. Washburn and S.T. Schicktanz. This still had been found to give an efficient separation of a 50 mole percent mixture of benzene and ethylene chloride, which have boiling points differing by only 3.42° C. Distillation of 1,820 ml of decene gave 28 fractions varying in volumes from 46 to 71 ml and a residue of 210 ml, representing 97.5 percent recovery. The boiling points and refractive indices of the various fractions indicated that the distilled material consisted primarily of 2 substances having approximately the following physical properties:

1st decene------bp −215 mm=110.8° C $n_D^{25}=1.4340$
2nd decene------bp −215 mm=116.8° C $n_D^{25}=1.4375$

[7] J. Am. Chem. Soc. 52, 1158 (1930).
[8] J. Am. Chem. Soc. 53, 3136 (1931); 54, 3706, 3710 (1932).
[9] J. Am. Chem. Soc. 52, 2547 (1930).
[10] Ind. Eng. Chem. 26, 94 (1934).
[11] Organic Syntheses, 12, 48.
[12] Thesis for Ph.D. degree, University of Maryland, 1929.
[13] BS J.Research 7,852(1931); 11,89(1933).

The first decene, when ozonized, yields acetaldehyde and a ketone boiling at 147.2° C at 766 mm, the semicarbazone of which melts at 147.6–8° C. The second decene, when ozonized, yields acetaldehyde and a ketone boiling at 154.4° C at 768 mm, the semicarbazone of which melts at 169.5° C. Thorough examination of fractions 2,5,13,19,25 and the residue failed to reveal the presence of any other decene. It was concluded that there are only 2 isomeric decenes formed, and that these isomers are present in equal proportions since the curve obtained by plotting the refractive index against the percentage distilled shows at approximately the midpoint a sharp rise between the 2 plateaus corresponding to the 2 decene isomers.

Inasmuch as acetaldehyde is formed by ozonolysis of both decenes, the group $=C=CH(CH_3)$ is present. Both ketones give the Hofmann test characteristic of methyl ketones, thereby extending the known portion of the decene molecules to $-C(CH_3)=CH(CH_3)$.

Oxidation of the methyl ketone obtained from the second decene to a seven-carbon acid with sodium hypobromite took place with good yields. The amide of the seven-carbon acid melts at 76.5° C. There are 17 possible structurally isomeric saturated seven-carbon acids. Beilstein lists the amides of 13 of these, only one of which melts in the neighborhood of the unknown amide. This acid is methyldiethylacetic acid whose amide has been reported by Haller and Bauer [14] to melt at 78–79° C. This acid was synthesized by the Grignard reaction from methyldiethylcarbinyl chloride and carbon dioxide, and was found to boil at the same temperature as the unknown seven-carbon acid, namely 104° C, at 13 mm. The amide melts at 78.5° C; a mixed melting point, however, shows a depression of approximately 30 degrees, indicating that the 2 acids are different.

Twelve of the seventeen possible structurally isomeric saturated eight-carbon methyl ketones are described in the literature. The boiling point of one of these and the melting point of its semicarbazone are very close to those of the unknown ketone. This is 3-methyl-3-ethylpentanone-2, which has been found by Nyberg [15] to boil at 153.5 to 154° C at 756 mm and to yield a semicarbazone melting at 168° C. This methyl ketone should yield on oxidation with sodium hypobromite the same seven-carbon acid that had already been synthesized by us. In view of the remarkable similarity in physical constants of the two ketones and acids, 3-methyl-3-ethylpentanone-2 was synthesized in order to check a possible rearrangement during the preparation of the acid. The method of Nyberg was used for the synthesis, involving the reduction of methylethylketone with magnesium amalgam and rearrangement of the symmetrical pinacol to the pinacolone with sulphuric acid at −10° C. The semicarbazone of the ketone fraction boiling from 153 to 155° C melts at 167.5° C; when mixed with the unknown semicarbazone the melting point shows a depression of about 30 degrees. Hence the two semicarbazones and the ketones are different substances.

Inspection of the data in the literature revealed that there were only three 8-carbon methyl ketones whose semicarbazones or derived seven-carbon acid amides were unknown. One of these three, namely 4,5-dimethylhexanone-2, has been made by Wheeler [16] and its

[14] Compt.rend. 148,127(1909).
[15] Ber. Deut. Chem. Ges. 55B,1960(1922).
[16] Thesis for M.S. degree, University of Maryland, 1931.

semicarbazone found to melt at 159 to 160.5° C. There remained only the following possible methyl ketones: 3,4,4-trimethylpentanone-2 and 4,4-dimethylhexanone-2. Evidence accumulated in the meantime by W. Gordon Rose[17] indicated that the ketone obtained from the lower boiling decene is 3,4,4-trimethylpentanone-2. It remained to prove that the second ketone is 4,4-dimethylhexanone-2.

The ketone was converted into the oxime by treatment with hydroxylamine and the resulting ketoxime was subjected to the Beckmann rearrangement by treatment with phosphorus pentachloride. The rearrangement proceeded with a 20 percent yield of a substituted acetamide, which was then hydrolyzed by a 1:1 aqueous syrupy phosphoric acid solution in a sealed tube at 230 to 240° C. Solid derivatives of the resultant amine were prepared with picryl chloride and benzenesulphonyl chloride. The picramide melts at 88 to 88.5° C. and the benzenesulphonamide at 59.5° C. The picramide and benzenesulphonamide of 1-amino-2,2-dimethylbutane were prepared synthetically in the following manner. Dimethylethylacetic acid was made through the Grignard reaction from tertiary amyl chloride and carbon dioxide. The acid was converted into the chloride with thionyl chloride and then into the amide by treatment with ammonium hydroxide. The amide was dehydrated with phosphorus pentoxide to form the nitrile which was then reduced to the amine with sodium and alcohol. The picramide and benzenesulphonamide were prepared in the usual manner. The picramide melts at 88 to 88.5° C and the benzenesulphonamide at 59.5° C. Mixed melting points with the derivatives obtained from the unknown ketone gave no depressions of the melting points. Hence the second ketone is 4,4-dimethylhexanone-2.

The action of 75 percent sulphuric acid on methylisopropylcarbinol at 80° C results, therefore, in the formation of 2 isomeric decenes, namely, 3,4,5,5-tetramethylhexene-2 and 3,5,5-trimethylheptene-2:

$$CH_3CH(CH_3)CHOHCH_3 \xrightarrow{H_2SO_4} CH_3C(CH_3)_2CH(CH_3)C(CH_3)=CHCH_3 + CH_3CH_2C(CH_3)_2CH_2C(CH_3)=CHCH_3$$

Details regarding the experimental procedure and analyses of the compounds are given elsewhere.[18]

III. DISCUSSION OF RESULTS

1. APPLICATION OF WHITMORE'S POLYMERIZATION THEORY

According to the theory of Whitmore[19] for the dehydration of alcohols, methylisopropylcarbinol would lose the hydroxyl group and become a positive organic ion, $CH_3CH(CH_3)\overset{+}{C}HCH_3$ (1). This positive fragment may lose a hydrogen ion from the isopropyl group to form trimethylethylene, $CH_3C(CH_3)=CHCH_3$ (2), or from the methyl group adjacent to the positive carbon to form isopropylethylene, $CH_3CH(CH_3)CH=CH_2$ (3). If the positive carbon of (1) has a greater attraction for electrons than the adjacent secondary

[17] Thesis for Ph.D. degree, University of Maryland, 1934.
[18] G. M. Kline. Thesis for Ph.D. degree, University of Maryland, 1934.
[19] J. Am. Chem. Soc. 54, 3274 (1932).

carbon, the hydrogen may shift with its electrons to form a new positive ion, $CH_3\overset{+}{C}(CH_3)CH_2CH_3$ (4). A shift of a methyl group in the case of (1) would not result in any change in structure of the positive ion. A loss of hydrogen from the newly formed ethyl group would produce trimethylethylene (2); loss of hydrogen from the adjacent methyl group would produce 1-methyl-1-ethylethylene, $CH_2{=}C(CH_3)$-CH_2CH_3 (5). Inasmuch as the carbon having the most electronegative groups attached to it has the least attraction for electrons, (4) would be expected to predominate rather than (1).

Union of (4) with (5) would yield a new positive organic ion, $CH_3CH_2C(CH_3)_2CH_2\overset{+}{C}(CH_3)CH_2CH_3$ (6). Loss of a hydrogen ion from the ethyl group would be expected as in the case of methylethylneopentylcarbinol,[20] and would form 3,5,5-trimethylheptene-2, $CH_3CH_2C(CH_3)_2CH_2C(CH_3){=}CHCH_3$ (7), observed as one of the products. Union of (4) with (2) would yield another positive ion, $CH_3CH_2C(CH_3)_2CH(CH_3)\overset{+}{C}(CH_3)_2$ (8). In order to account for the 3,4,5,5-tetramethylhexene-2 observed as the second product of the reaction investigated, (8) would have to undergo a shift of a methyl group to form $CH_3CH_2\overset{+}{C}(CH_3)CH(CH_3)C(CH_3)_2CH_3$ and then loss of hydrogen from the ethyl group to yield the observed olefin, $CH_3CH{=}C(CH_3)CH(CH_3)C(CH_3)_2CH_3$ (9). However, the evidence accumulated by Whitmore in his investigation of the dehydration of various alcohols indicates that a positive fragment such as (8) would liberate the hydrogen ion adjacent to the positive carbon to form 2,3,4,4-tetramethylhexene-2.

2. PROPOSED ACTIVATION MECHANISM

If the explanation of the formation of the above products is sought in a theory somewhat analogous to that proposed by Rice [21] for the thermal decomposition of organic compounds from the standpoint of free radicals, the mechanism is much simpler. In effect at least the molecule of trimethylethylene behaves as though it were activated in the following manner: $CH_3^-\ {}^+C(CH_3){=}CH(CH_3)$. The positive and negative signs are used to indicate the relative electronegativities as defined by Kharasch [22] and are not intended to indicate ionization. The addition of these two fragments to the double bond of a nonactivated molecule of trimethylethylene would take place in accordance with the relative electronegativities as follows:

$$(CH_3)_2\overset{+}{C}{=}\overset{-}{C}HCH_3 + CH_3^-\ {}^+C(CH_3){=}CHCH_3 \rightarrow CH_3C(CH_3)_2CH\text{-}(CH_3)C(CH_3){=}CHCH_3$$

This is one of the observed products, namely 3,4,5,5-tetramethylhexene-2. The addition of the two fragments to the double bond of 1-methyl-1-ethylethylene would take place as follows:

$$C_2H_5(CH_3)\overset{+}{C}{=}\overset{-}{C}H_2 + CH_3^-\ {}^+C(CH_3){=}CHCH_3 \rightarrow C_2H_5C(CH_3)_2CH_2C\text{-}(CH_3){=}CHCH_3$$

[20] J. Am. Chem. Soc. 54, 4011 (1932); 55, 3732 (1933).
[21] J. Am. Chem. Soc. 53, 1959 (1931).
[22] J. Am. Chem. Soc. 48, 3130 (1926).

This is the other observed product, namely 3,5,5-trimethylheptene-2. If this mechanism is correct, trimethylethylene and 1-methyl-1-ethylethylene are produced by the dehydration of methylisopropylcarbinol in the ratio 3:1. This addition of the activated olefin molecule to a double bond is similar to the addition of RMgX to a carbonyl group $=C=O$ to yield $=C(R)-OMgX$, and to the catalyzed hydrogenation of a double bond.

3. APPLICATION OF THE ACTIVATION MECHANISM TO DIISOBUTYLENE

The products formed by the polymerization of isobutylene can be predicted by the same mechanism. From a consideration of the relative electronegativities involved or of the relative calorie strengths of the C-H and C-C bonds, isobutylene would be expected to behave as $CH_3^- {}^+C(CH_3)=CH_2$ rather than $H^+ {}^-CH=C(CH_3)_2$. The products observed in the formation of the dipolymer can be accounted for on the basis of the "activation" taking place 80 percent in the first sense and 20 percent in the second sense with subsequent addition to a molecule of isobutylene:

$$(CH_3)_2\overset{+}{C}=\overset{-}{C}H_2+CH_3^- {}^+C(CH_3)=CH_2 \rightarrow CH_3C(CH_3)_2CH_2C(CH_3)=CH_2 \quad (10)$$

$$(CH_3)_2\overset{+}{C}=\overset{-}{C}H_2+H^+ {}^-CH=C(CH_3)_2 \rightarrow CH_3C(CH_3)_2CH=C(CH_3)_2 \quad (11)$$

The mechanism postulated by Whitmore is rather unsatisfactory in this case, also, since to obtain the above products according to his theory it is necessary to liberate a hydrogen ion from a methyl group in preference to a neopentyl group, whereas he found in a study [23] of the dehydration of 4,4-dimethylpentanol-2 that the liberation of the hydrogen occurred from the neopentyl group rather than the methyl group in the ratio 4.5:1.

4. APPLICATION OF THE ACTIVATION MECHANISM TO TRIISOBUTYLENE

The formation of the triisobutylenes provides an interesting confirmation of the activation mechanism. In this case there are 3 olefins present which may be activated, the original isobutylene and the 2 dimers (10) and (11). Isobutylene activated as $CH_3^- {}^+C(CH_3)=CH_2$ uniting with dimer (10) would form $CH_3C(CH_3)_2CH_2C(CH_3)_2CH_2C(CH_3)=CH_2$ (12) and with dimer (11) would form $CH_3C(CH_3)_2CH[C(CH_3)_3]C(CH_3)=CH_2$ (13). Isobutylene activated as $H^+ {}^-CH=C(CH_3)_2$ uniting with dimer (10) would form $CH_3C(CH_3)_2CH_2C(CH_3)_2CH=C(CH_3)_2$ (14) and with dimer (11) would also form trimer (14). Dimer (10) activated as $CH_3^- {}^+C(=CH_2)CH_2C(CH_3)_3$ uniting with isobutylene would form $CH_3C(CH_3)_2CH_2C(=CH_2)CH_2C(CH_3)_3$ (15), and activated as $H^+ {}^-CH=C(CH_3)CH_2C(CH_3)_3$ uniting with isobutylene would form $CH_3C(CH_3)_2CH_2C(CH_3)=CHC(CH_3)_3$ (16). Dimer (11) activated as $CH_3^- {}^+C(CH_3)=CHC(CH_3)_3$ uniting with isobutylene would form trimer (16), and activated as $H^+ {}^-C[C(CH_3)_3]=C(CH_3)_2$ uniting with

[23] J. Am. Chem. Soc. 55,4194(1933).

isobutylene would form $CH_3C(CH_3)_2C[C(CH_3)_3]=C(CH_3)_2$ (17). Of these 6 isomers (12), (14), (15), and (16) involve the dimer which makes up 80 percent of diisobutylene and they would, therefore, be expected to predominate in triisobutylene. The presence of these 4 isomers in triisobutylene has been reported by Whitmore [24] without a statement as to the proportions of each. When it is considered that there are 2,281 isomers with the empirical formula $C_{12}H_{24}$, as calculated by Henze and Blair,[25] the value of a simple mechanism which permits the prediction of the products of polymerization of simple olefins becomes evident.

5. POSSIBLE TAUTOMERIC EQUILIBRIUM

The C-H bond is approximately 22,000 calories stronger than the C-C bond and objection may be made, therefore, to the postulation of a break in the C-H bond in isobutylene to yield 20 percent of the dimer reaction products. However, it has been suggested to us by S. F. Acree of this Bureau that a tautomeric relation may exist between dimers (10) and (11) through a shift of the double bond from the 1 to the 2 position.[26] A similar tautomeric relationship between trimers (12) and (14), and (15) and (16) is possible. Evidence of such a tautomeric equilibrium could be sought by subjecting one of the dimers to the conditions resulting in their formation from isobutylene and examining the product for the presence of the other isomer. It is recognized however, that the energy of activation present in the dimer at the instant of its formation may be a necessary factor in this shift of the double bond, and that activation of the inactive dimer molecules may not take place under the same conditions that supply the necessary energy to the smaller monomer molecules. It is noteworthy that the products of such a tautomeric shift of the double bond were not observed with the diamylenes studied by the authors and that the products found result from the breaking of C-C bonds rather than C-H bonds.

6. LABILE HYDROGEN THEORY

Attempts have been made to explain the formation of polymers of olefins on the basis of a labile hydrogen theory.[27] Thus Carothers [28] formulates the mechanism for the polymerization of vinyl compounds as follows:

$$RCH=CH_2+RCH=CH_2\rightarrow RCH_2CH_2C(R)=CH_2$$

$$RCH_2CH_2C(R)=CH_2+RCH=CH_2\rightarrow RCH_2CH_2CH(R)CH_2C(R)=CH_2, \text{ etc.}$$

However, according to our mechanism the predominant reaction in the first stage would be:

$$R\overset{+}{C}H=\overset{-}{C}H_2+R^{-}\,{}^{+}CH=CH_2\rightarrow R_2CHCH_2CH=CH_2$$

[24] Ind. Eng. Chem. 26,94(1934).
[25] J. Am. Chem. Soc. 55,685(1933).
[26] Ber. Deut. Chem. Ges. 36, 2003(1903).
[27] J. Am. Chem. Soc. 53, 356(1931).
[28] Chem. Rev. 8, 353(1931).

and in the second stage would be:

$$R_2CHCH_2\overset{+}{C}H{=}\overset{-}{C}H_2 + R^{-}\,{}^{+}CH{=}CH_2 \rightarrow R_2CHCH_2CH(R)CH_2CH{=}CH_2$$

Activation of the monomer as $H^{+}\,{}^{-}CH{=}CHR$ would also be expected to a greater extent than in the case of isobutylene considered above and would give rise to the dimer $CH_3CH(R)CH{=}CHR$. The trimers which would probably be formed in the polymerization of such a compound can be deduced by the same procedure used for isobutylene. Propylene, $CH_3CH{=}CH_2$, furnishes a particularly advantageous type compound for the study of such polymerization since it is the simplest molecule containing C-C as well as C-H linkages adjoining the double bond. We hope to present experimental evidence regarding the polymerization of propylene with sulphuric acid at a later date.

WASHINGTON, August 25, 1934.