

## POLYMERIZATION OF OLEFINES.\*

BY R. VAN WINKLE.

Within the past few years considerable work has been accomplished in studying the pharmacological action of the lower members of the hydrocarbons of the ethylene series. Propylene, the second member of this series, has offered great possibilities as a new and valuable anæsthetic. In the use of the latter, as an anæsthetic, certain undesired results have been observed which are attributed to impurities present in small amounts. It is thought that higher members of the ethylene series of hydrocarbons (*i. e.*, isobutylene, *n*-butylene, etc.) comprise these impurities. The ethylene hydrocarbons are prepared by the dehydration of the corresponding alcohols, and in the case of propylene, the isopropyl alcohol used had been obtained in the highest possible state of purity known to modern chemistry without producing the desired results. Accordingly it resolved into a problem of removing the impurities from the final product, propylene, and it is in connection with the latter that the following work has been carried on.

Gurwitsch in his studies on adsorption found that amylene and pinene were rapidly polymerized by gently heated Floridin, a commercial silicate, used in decolorizing oil products. Lebedew and Filanenko, two Russian chemists, next took up the study and investigated quite thoroughly the field of polymerization by the above substance. They experimented with numerous unsaturated hydrocarbons but especially with those of the ethylene series and as a result set forth the following generalizations:

1. Of the ethylene compounds only those polymerize in presence of activated Floridin which are derivatives of asymmetrical doubly or triply substituted ethylenes ( $RR'C=CH_2$ ,  $RR'C=CHR''$ ).
2. Simply substituted ethylenes and symmetrical doubly and triply substituted compounds do not polymerize.
3. The above rules apply also to diethylenes.

From these generalizations we are led to believe that propylene, a simply substituted ethylene, will not be polymerized by activated Floridin while an asymmetrical doubly substituted ethylene, like isobutylene, will readily tend towards polymerization. By the use of activated Floridin a method suggested itself for the removal of some of the impurities from propylene.

## EXPERIMENTAL WORK.

As a matter of courtesy we wish to state that the literature work as well as the preliminary experiments were carried out by other members of the laboratory prior to our taking over this particular phase of the problem.

## PROPYLENE.

The activated Floridin used was prepared by heating the commercial Floridin at a fairly high temperature over a period of time as suggested by Lebedew. The propylene was manufactured by a catalytic process of alcohol dehydration and two pounds of the latter with one pound of activated Floridin were stored in suitable cylinders for observation purposes. At the end of two months several

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of these cylinders were opened and the Floridin examined. The latter was found to be saturated with a liquid and in some cases even a small amount of free liquid could be decanted off. The amount of polymers formed was far in excess of that which might be formed from the small amount of impurities known to be present. It was thought at the time that a combination of one molecule of propylene with one molecule of a higher member of the series of ethylene hydrocarbons might have taken place or else the propylene might have polymerized itself. The latter, however, was not in accord with Lebedew's generalization as previously stated. A distillation under normal pressure showed a portion of the liquid boiling around 70° C., another portion around 100° C. and a higher boiling residue remaining. According to Mulliken, substances of the empirical formula  $(C_3H_6)_2$  the same as a dimer of propylene, have the following boiling points:

Dimethyl ethyl ethylene	66° C.	Methyl ethyl propylene	69.5-71° C.
S methyl propyl ethylene	68° C.	Tetra methyl ethylene	73° C.
Butyl ethylene	69° C.		

Likewise substances of an empirical formula  $(C_3H_6)_3$ , the same as a trimer of propylene, boil around 100° C. From the above we were fairly sure that we were dealing with polymers of propylene. No further work was done until a year following the beginning of the experiment. At this time some more cylinders were opened and it was noticed that each contained several hundred cubic centimeters of polymer mixture. A portion of this when subjected to distillation at normal pressure yielded no distillate around 70° C., and only a small portion coming over between 100° C. and 150° C. A liter of the polymers was obtained by extracting the Floridin in several cylinders with petroleum ether and distilling off the latter at a low temperature. The resulting polymer mixture was put through a process of repeated fractional distillation under diminished pressure with the following results.

Fraction I	15%	Boiling range	35.5-37.5° C./7 mm.
Fraction II	30%	Boiling range	60-64.5° C./7 mm.
Fraction III	15%	Boiling range	82-85° C./3 mm.
Residue	40%	Higher boiling polymers	

As a means of identification of the various fractions our intention was to form the di-brom derivatives on the assumption that each molecule contained but one double bond. We met with difficulty here, in that in every case substitution of bromine occurred long before addition of the same substance could possibly be complete. It was next decided to determine the molecular weight of the fractions by determining the lowering of the freezing point of pure benzene. The latter was obtained by low-temperature crystallization from chemically pure benzene. The molecular freezing point depression constant for benzene was taken, as given by Landolt Börnstein, as 51.2.

*Molecular Weight of Fraction I.*

Wt. of benzene.....	9.5814 Gm.
Wt. of polymer.....	0.1932 Gm.
Freezing point lowering....	0.77° C.
Mol. weight determined....	134
Mol. weight calculated for a trimer of propylene.....	126

*Molecular Weight of Fraction II.*

Wt. of benzene.....	7.0447 Gm.
Wt. of polymer.....	0.2420 Gm.
Freezing point lowering....	1.03° C.
Mol. weight determined....	171
Mol. weight calculated for a tetramer of propylene....	168

*Molecular Weight of Fraction III.*

Wt. of benzene.....	9.0534 Gm.
Wt. of polymer.....	0.3417 Gm.
Freezing point lowering....	0.89° C.
Mol. weight determined....	214
Mol. weight calculated for a pentamer of propylene....	210

*Mean Molecular Weight of Residue.*

Wt. of benzene.....	9.1402 Gm.
Wt. of residue.....	0.3581 Gm.
Freezing point lowering....	0.61° C.
Mol. weight determined....	328

This corresponds closely to the molecular weight of an octamer of propylene (336) and would indicate that the residue is composed of several polymers of propylene higher than a pentamer.

*Note.*—Control cylinders run at the same time containing propylene but no activated Floridin showed no polymer or liquid formation over a year's period.

## ISOBUTYLENE.

In his work on isobutylene, Lebedew states that polymerization of the latter with activated Floridin takes place very readily. His experiment was repeated in our laboratory and by distillation at normal pressure of the polymer mixture formed it was indicated that a dimer, trimer and higher polymers were present. In this work a very short column of activated Floridin (five inches) had been used. It was decided to prepare the polymers on a larger scale and in so doing we used a twenty-four-inch column of the Floridin. Our isobutylene was prepared from tertiary butyl alcohol and before passing into the well-cooled Floridin tower it was washed free from any unchanged alcohol and then dried. The receiving flask for the isobutylene polymers was kept well chilled to prevent any loss of the lower boiling members due to volatilization. In carrying out the experiment we found that a slight pressure developed in the system would tend to increase the rate of reaction. Several liters of isobutylene polymers were obtained and a portion subjected to repeated fractional distillation in vacuo with the following results:

Fraction I	62.5%	Boiling range	43–46° C./7 mm.
Fraction II	13.3%	Boiling range	75–79° C./5 mm.
Residue	24.2%	Higher boiling polymers	

The molecular weights of these fractions were determined as described under propylene.

*Molecular Weight of Fraction I.*

Wt. of benzene.....	5.9512 Gm.
Wt. of polymer.....	0.2142 Gm.
Freezing point lowering....	1.12° C.
Mol. weight determined....	164
Mol. weight calculated for a trimer of isobutylene....	168

Freezing point lowering....	0.585° C.
Mol. weight determined....	222
Mol. weight calculated for tetramer of isobutylene....	224

*Mean Molecular Weight of Residue.*

Wt. of benzene.....	9.4859 Gm.
Wt. of residue.....	0.2985 Gm.
Freezing point lowering....	0.49° C.
Mol. weight determined....	328

*Molecular Weight of Fraction II.*

Wt. of benzene.....	8.3184 Gm.
Wt. of polymer.....	0.2110 Gm.

The molecular weight of a hexamer of isobutylene is 336 and accordingly the residue must contain several polymers of isobutylene higher than a tetramer.

## CONCLUSIONS.

1.—It has been shown that although propylene is stated by Lebedew not to polymerize in the presence of activated Floridin, it does polymerize in the presence of the latter if kept under pressure.

2.—The factors influencing the polymerization of olefines by activated Floridin are:

(a) *Temperature*.—Inasmuch as the reaction is exothermic and a large amount of heat is liberated, proper cooling of the activated Floridin is essential for best results.

(b) *Pressure*.—Pressure was essential to polymerize a simply substituted ethylene, namely propylene, and in the case of isobutylene, an asymmetrical doubly substituted ethylene, which polymerizes readily at ordinary pressure, the polymerization reaction is increased if the system is put under pressure.

(c) *Time of Contact with Activated Floridin*.—Propylene under pressure with activated Floridin for two months had formed some dimer while at the end of year no dimer was present. Isobutylene when passed through a short column of activated Floridin formed some dimer but when the length of the column was materially increased only higher polymers were found.

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A DISCUSSION OF THE PHARMACOPŒIAL SPECIFICATIONS  
FOR CRESOL.\*

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After the publication of the U. S. P. X a certain agitation was manifested to have either the present specifications for U. S. P. Cresol changed or else to have a new high boiling Cresylic Acid incorporated into the book in addition to the present Cresol. The discussion was opened by manufacturers of saponified cresol solutions from cresylic acids of higher boiling range than that outlined in the U. S. P. Their principal arguments for the change are four in number, namely: (1) Cresylic Acids of higher boiling range than 195–205° C. possess greater germicidal values than U. S. P. Cresol, (2) they are less corrosive to tissues, (3) they are cheaper and (4) there is a greater available supply of them on the market. Certainly, if true, these are a very valid set of arguments. Since Solution Cresol Compound, U. S. P. now enjoys quite an extensive use as a germicide by members of the medical profession especially, the question of a change in its specifications will no doubt have to be considered before the publication of the next U. S. P. A large number of saponified cresol solutions purporting to be U. S. P. products but which do not contain Cresol corresponding to the specifications of the U. S. P. X have appeared on the market. In order to maintain the dignity of the U. S. P. as a legal standard it becomes necessary to have any solutions erroneously labeled as U. S. P. removed from the market or else to have the U. S. P. specifications changed to include them. It has not been the policy of U. S. P. revision com-

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