Oxidation of Poly(dimethylbutadiene) Popcorn Polymer

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ABSTRACT

Poly(dimethylbutadiene) popcorn polymer oxidizes readily in the presence of oxygen at room temperature. Quantitative data are presented for the production of the major volatile product, 2,5-hexanedione, as well as for the secondary products: water, acetic acid, and acetaldehyde. Three reaction mechanisms formerly proposed for polyisoprene oxidation are considered for their applicability to poly(dimethylbutadiene) popcorn oxidation. Of these, one that assumes the formation of a Bevilacqua-type peroxyalkoxy radical followed by hydrogen abstraction to form an alcohol group, double bond migration, formation of a peroxide radical adjacent to the alcohol, then elimination of a hydroxy radical and scission, can explain the experimental data.

INTRODUCTION

Kondakoff [1] first reported the formation of poly(dimethylbuta-diene) (PDMB) popcorn polymer in 1900, and the spontaneous polymerization of dimethylbutadiene to popcorn polymer was used by the Germans in World War II to make methyl rubber H by seeding

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dimethylbutadiene monomer with PDMB popcorn seeds. Wibaut [2] grew PDMB seeds in the presence of dimethylbutadiene vapor. He observed no seed growth when he placed polyisoprene popcorn in dimethylbutadiene vapor; however, this was the method used to grow PDMB seeds in this work. Bevilacqua [3] reported that 2,5-hexane-dione was a product from the oxidation of poly(dimethylbutadiene).

The purpose of the present work was to study the oxidation of PDMB popcorn quantitatively and to elucidate the mechanism of the autoxidation reaction. Popcorn polymers are uniquely suited to these studies due to their high purity. The PDMB popcorn was grown in the absence of air, water, inhibitors, catalysts, cross-linking agents, or other contaminating species. It is thus possible to observe features of the oxidation that may be obscured when other polymer sources are used.

EXPERIMENTAL

PDMB popcorn was grown anerobically at 60°C in the manner previously described for polyisoprene popcorn polymer [4, 5]. The first generation PDMB seeds were initially prepared by seeding a small sample of polyisoprene popcorn (PIP) above dimethylbutadiene vapor. Small portions of the first generation seeds when grown above additional dimethylbutadiene monomer (Aldrich Chemical Co.) pro-duced second generation seeds. Second and third generation seeds were used for the reported experiments. All handling of the polymer was done in the inert atmosphere of a glove box that was continuously flushed with dry nitrogen.

Volatile impurities, consisting mainly of mono-, di-, and trimers, were removed from the PDMB popcorn by flushing with a stream of dry helium for 300 h. The apparatus used for both the helium flushing and the room temperature oxidations has been described [4]. Each 4 to 6 h oxidation period was followed by an 18 to 20 h helium flush to remove the volatile reaction products.

Volatile oxidation products were collected at Dry-Ice temperature and analyses were made using a Hewlett-Packard model 7620A chromatograph equipped with 10 ft, 1/8 in. copper tubing columns filled with Porapak QS (80-100 mesh). The oven temperature was programmed as follows: 100° for 2 min, increased 30°/min to 130° and held for 2 min, increased 30°/min to 180° and held for 2 min, and then increased 30°/min to 240° and held for 30 min. Peak areas were measured by an integrator and compared to areas obtained from standard samples. The results of three or four analyses were aver-aged for each point graphed.

Identifications of the products were obtained by mass spectrography, retention times of known compounds, and NMR. Analyses of the helium-flush products were made by trapping the samples in cooled NMR tubes containing carbon tetrachloride as they exited the VPC apparatus.

Spectra were obtained using signal averaging on an XL-100 NMR instrument.

EXPERIMENTAL RESULTS

Helium flushing of the PDMB popcorn after removal from the sealed tubes in which it had been grown produces between 0.5 and 0.9% by mass of volatile products. In addition to small amounts of monomer and traces of a number of low molecular mass compounds, three higher mass compounds were separated by chromatography. The first of these was identified as the dimer, Structure I:

I
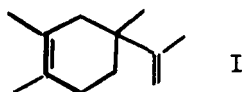
The other two had molecular masses corresponding to trimers. Two Diels-Alder trimers are possible, Structures II and III:

II   III

The presence of Trimer II has positively been identified by NMR. The identity of Trimer III, however, could not be definitely established.

The rapid oxidation of PDMB popcorn is illustrated in Fig. 1 where millimoles of oxygen reacted per mole of initial monomer units is plotted versus time. The oxidation is accompanied by an increase in polymer mass and a loss in volume. After an oxidation period of 24 h, the polymer occupies less than half the original volume, becomes very tacky, and has a glassy appearance but is still white in color. After more extended oxidation, the polymer collapses completely to a viscous, orange-colored gel. This highly oxidized polymer is soluble in acetone and can be reprecipitated by the addition of water.

The amount of oxygen reacted with the polymer was determined by equating it to the sum of the increased mass of the polymer and the mass of the collected products. For example, in one oxidation experiment, 12.7628 g of helium-flushed polymer increased in mass 0.0235 g after exposure to a-20 mL/min stream of dry oxygen for 16 h at room temperature. During this time period, 0.2741 g of condensable products were collected; hence a total of 0.2976 g of oxygen had reacted. Any trace amounts of noncondensable gases were neglected in the calculations. From the quantitative data obtained after each oxidation
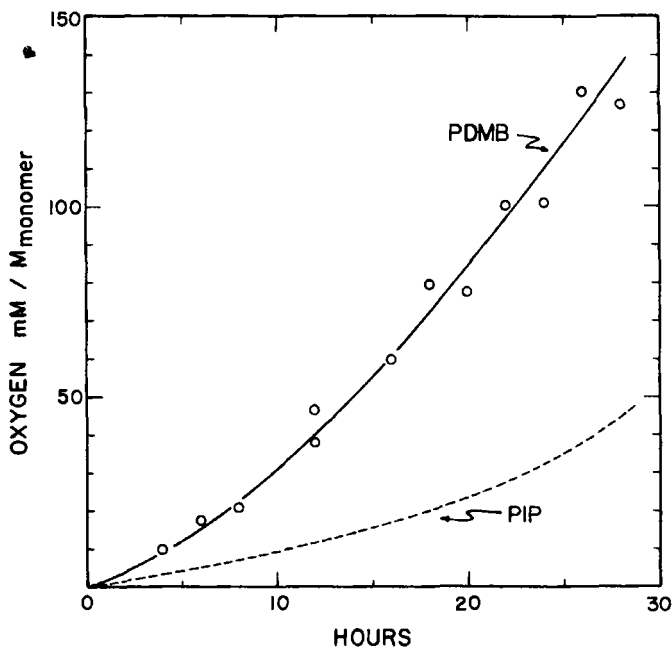
FIG. 1. Oxidation rate for PDMB popcorn polymer.

period, the amount of the reacted oxygen that was contained in the
condensed reaction products could be calculated (that is, in the water,
hexanedione, acetic acid, acetaldehyde, and Compound A considered
as a dione). Following the 16-h oxidation, the oxidized polymer con-
tained 1.7% oxygen by mass. This corresponds to approximately one
oxygen atom for every 11 mer units. After 28 h of oxidation the
oxygen content was 3.8% or the equivalent of one oxygen atom for
every 5 mer units.

Figure 2 is a chromatograph of the volatile products obtained
during the first 4 h of PDMB popcorn oxidation; Fig. 3 shows the
product distribution for the 20 to 24-h oxidation interval. The num-
bers below the curves indicate the changes in instrument sensitivity
and the relative peak-area integrations are shown for the primary
products normalized to hexanedione = 1000. With the exception of the
major product, 2,5-hexanedione, all other compounds were present
in very small amounts. The products studied quantitatively were 2,5-
hexanedione, water, acetic acid, acetaldehyde, and an unidentified
Compound A. A comparison of Figs. 2 and 3 shows that some formal-
dehyde and formic acid were detected; the rate of formation of formic
acid increased during the latter oxidation periods. While the rate of
formation of water doubled, the rate of formation of the other prod-
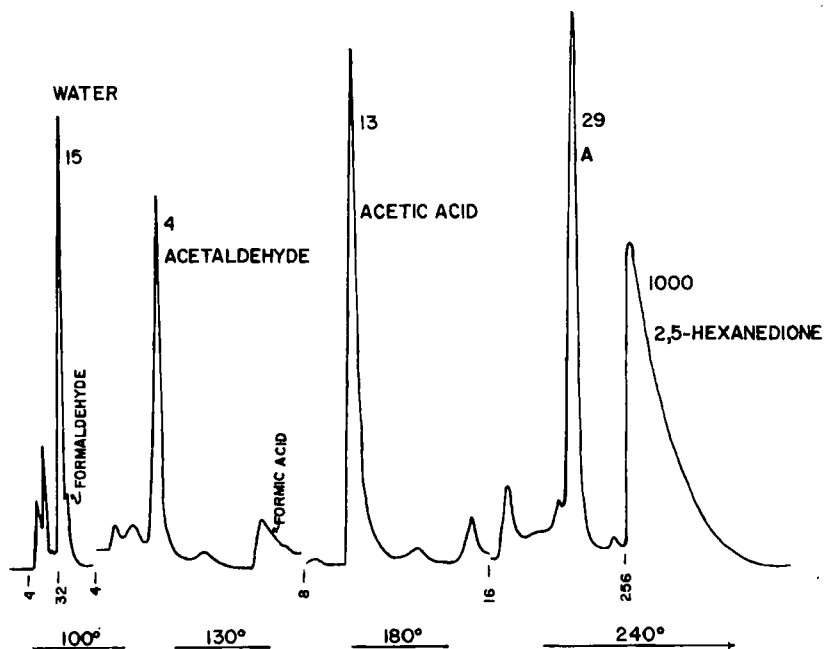ucts remained approximately the same.

FIG. 2. Chromatogram of volatile products collected during the first 4 h of poly(dimethylbutadiene) popcorn polymer autoxidation.

The millimoles of 2,5-hexanedione produced per mole of original monomer is plotted as a function of time in Fig. 4, and as a function of the millimoles of oxygen reacted per mole of initial monomer in Fig. 5. The production of 2,5-hexanedione increases linearly with the amount of oxygen reacted. Approximately 1 mol of 2,5-hexanedione is produced for every 5 mol of reacted oxygen.

Data for water are shown in Figs. 6 and 7. The rate of formation of water increases quite rapidly with time, but when the data are plotted showing the amount of water produced as a function of oxygen reacted, it is seen that, analogous to 2,5-hexanedione, the increase is approximately linear with the amount of oxygen reacted.

Acetic acid and acetaldehyde follow similar patterns (Figs. 8 and 9), the rates of production being linear functions of the amount of oxygen reacted. Approximately 2.6 mol of acetic acid appeared for each mole of acetaldehyde.
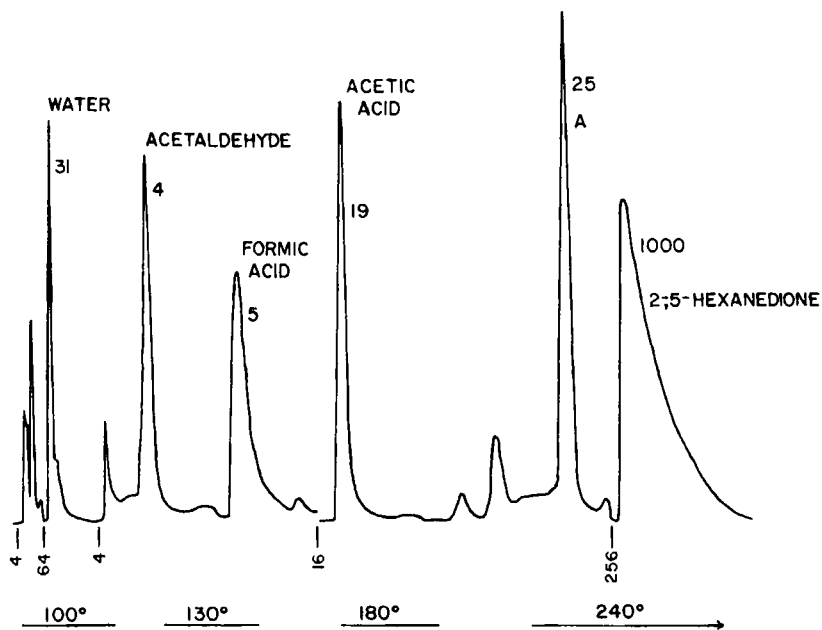
FIG. 3. Chromatogram of volatile products collected during the 20 to 24 h period of poly(dimethylbutadiene) popcorn polymer autoxidation.
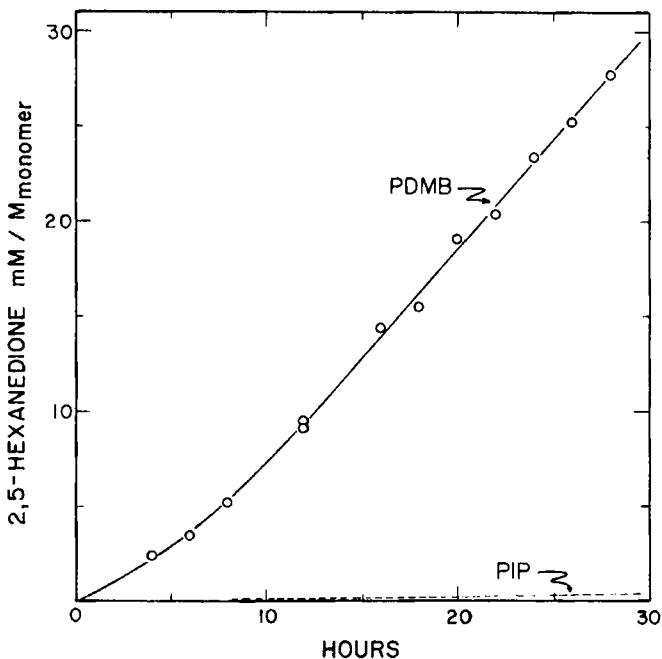

FIG. 4. Rate of 2,5-hexanedione production during the early stages of PDMB popcorn polymer autoxidation.
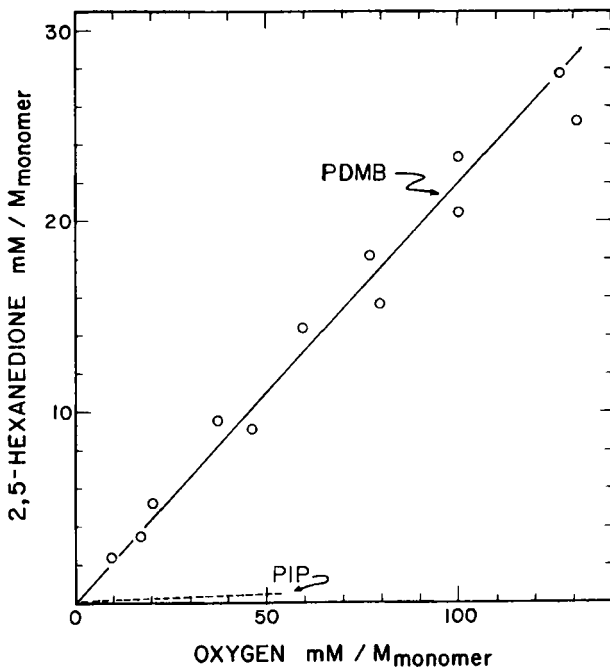
FIG. 5. Rate of 2,5-hexanedione formation as a function of oxygen consumed during the early stages of PDMB popcorn polymer autoxidation.

DISCUSSION AND CONCLUSIONS

It is logical to assume that the oxidation mechanism applicable to polyisoprene autoxidation would also be applicable to poly(dimethylbutadiene). Much work has been done in an attempt to understand the autoxidation of polyisoprene and numerous schemes have been proposed for the mechanism of the reaction. Three of the most prominent of these schemes will be considered for their applicability to the oxidation of PDMB.

Bolland and Hughes [6] found a cyclic peroxyhydroperoxide as one of the main oxidation products of squalene, a model for polyisoprene, and Bateman [7] proposed this structure as the intermediate that leads to the scission step in polyisoprene oxidation. If the same mechanism applies to PDMB oxidation, the cyclic peroxyhydroperoxide would be as shown in Structure IV.

Bevilacqua [8], to explain levulinaldehyde as a product from polyisoprene oxidation, proposed a cyclic diperoxy radical formed
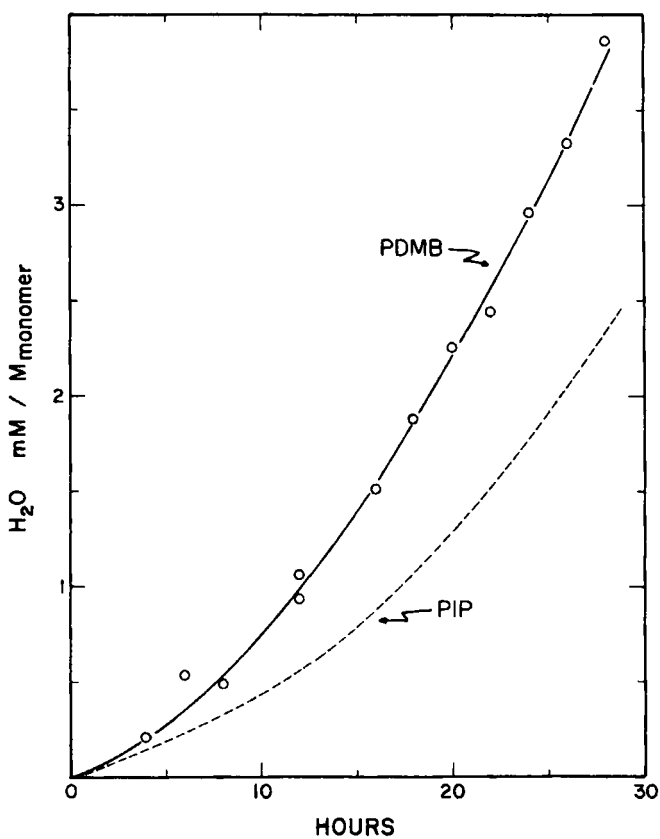
FIG. 6. Rate of water formation during the early stages of PDMB popcorn polymer autoxidation.

FIG. 7. Rate of water formation as a function of oxygen consumed during the early stages of PDMB popcorn polymer autoxidation.

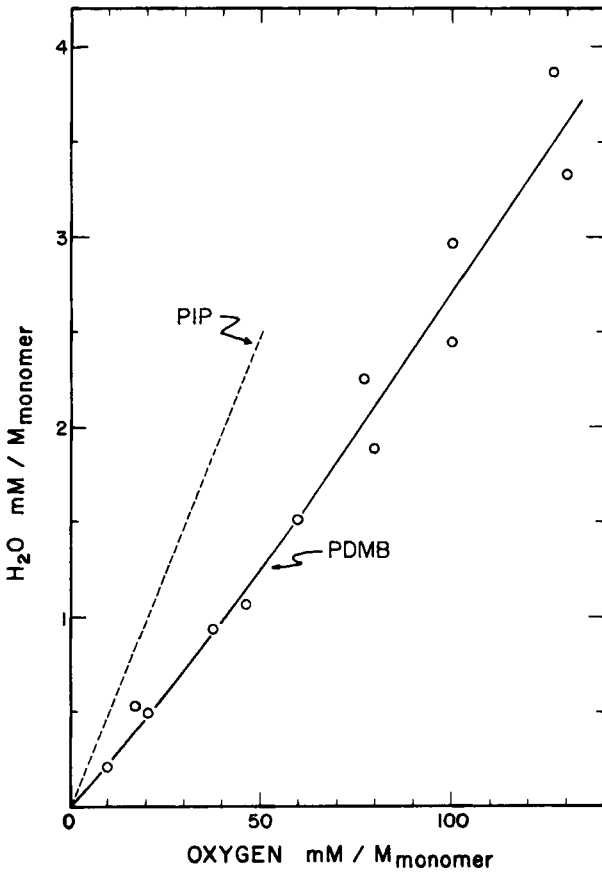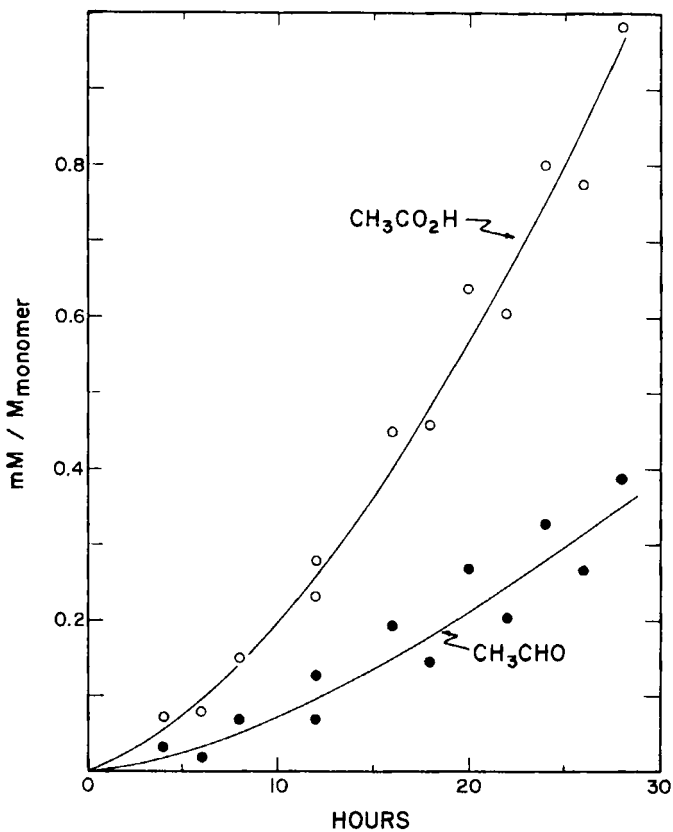FIG. 8. Rates of acetic acid and acetaldehyde production during the early stages of PDMB popcorn polymer autoxidation.
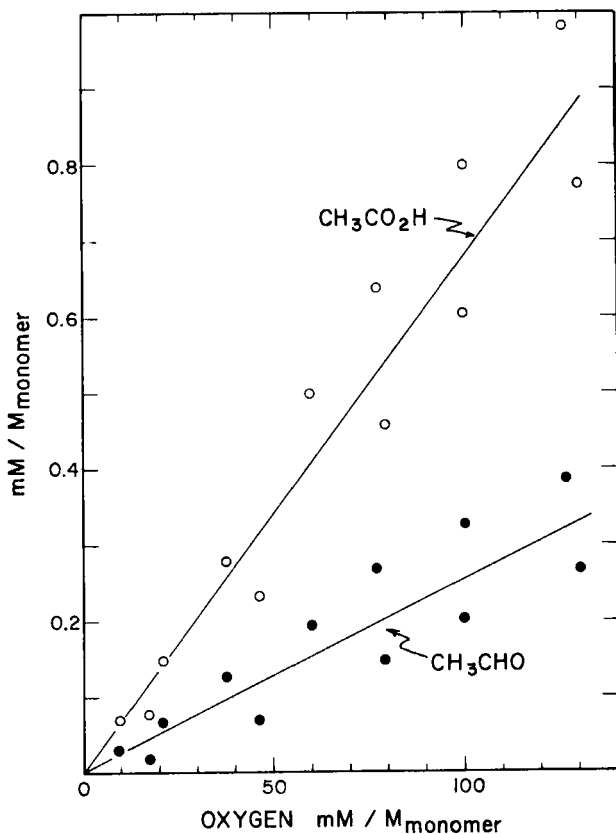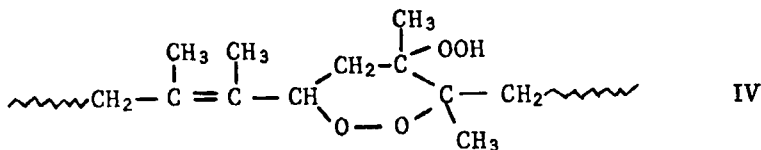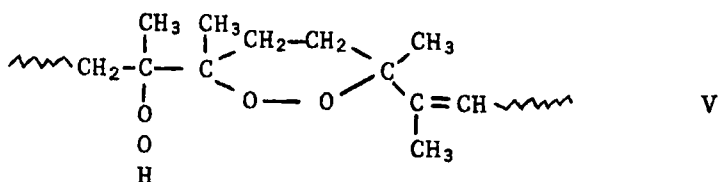
FIG. 9. Rates of acetic acid and acetaldehyde production as a function of the amount of oxygen consumed during the early stages of PDMB popcorn polymer autoxidation.

$$\text{\char`\~\char`\~\char`\~} CH_2 - \underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C} - CH \begin{array}{c} \nearrow CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \nearrow OOH \\ \diagdown O - O \diagup \underset{\underset{CH_3}{}}{C} - CH_2 \text{\char`\~\char`\~} \end{array} \qquad IV$$

after the displacement of an isoprene double bond. Adapting this to
PDMB oxidation yields Structure V:

$$\text{\char`\~\char`\~} CH_2 - \underset{\underset{\underset{\underset{H}{O}}{O}}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \begin{array}{c} CH_2 - CH_2 \diagdown \\ \diagdown O - O \diagup \end{array} \underset{\underset{\underset{CH_3}{|}}{C} = CH \text{\char`\~\char`\~}}{\overset{\overset{CH_3}{}}{C}} \qquad V$$
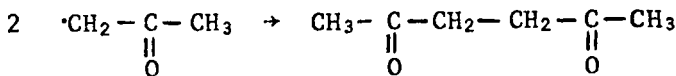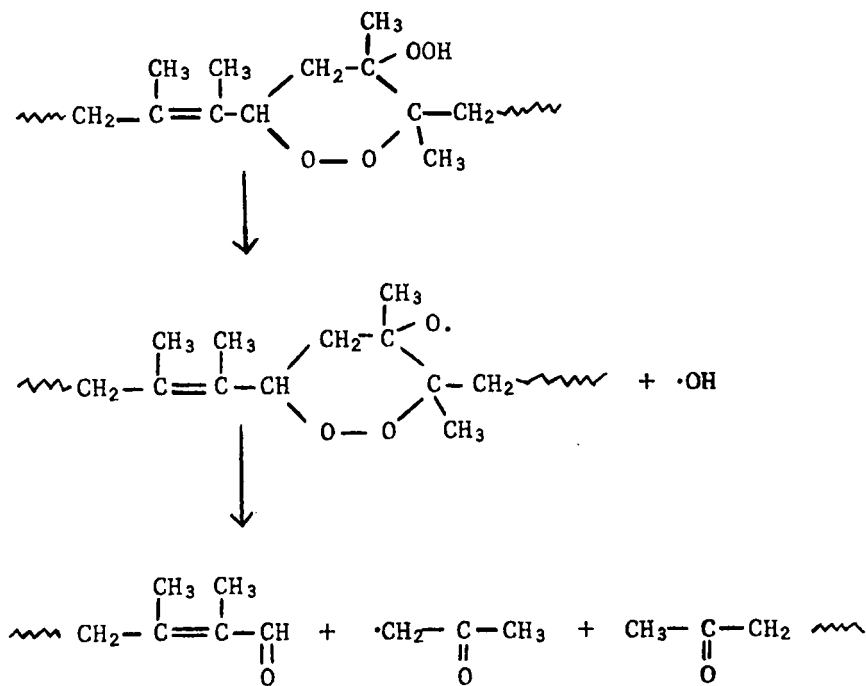
   Golub and Hsu [9] made a careful study of the thermal oxidation
of polyisoprene and the model compounds squalene and dihydro-
myrcene using carbon-13 and proton NMR. They concluded that both
the Bolland-Hughes and Bevilacqua structures are present in oxi-
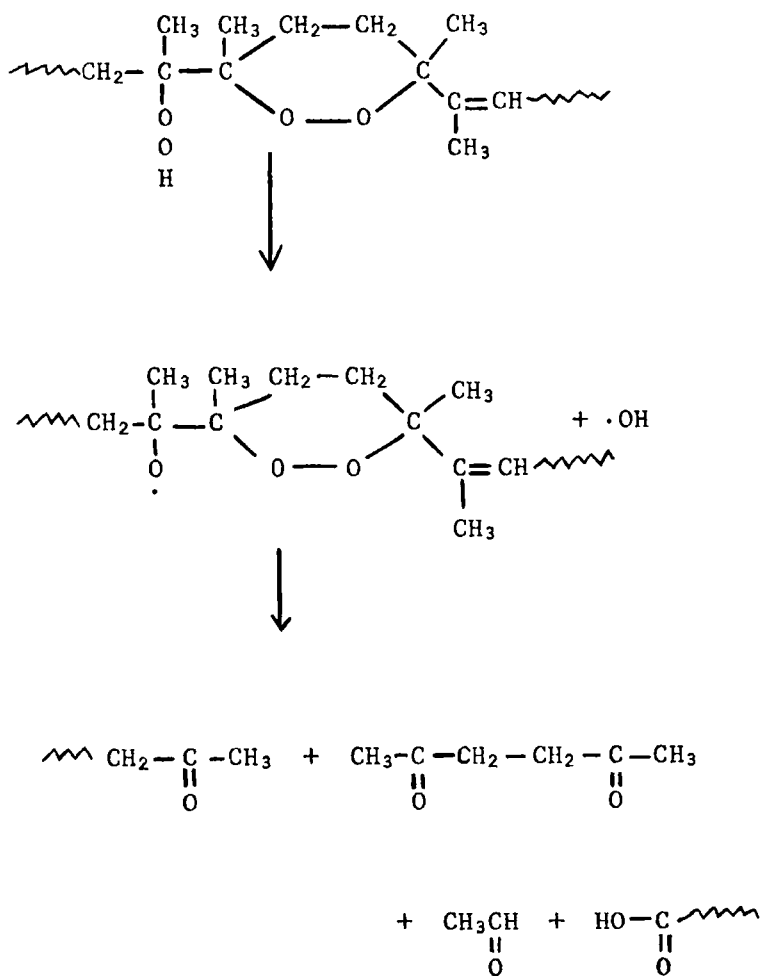dized polyisoprene but in some as yet undetermined ratio.
   Utilizing cyclic Intermediates IV and V for PDMB, two possible
mechanisms for the oxidative scission of PDMB are shown in
Schemes A and B.
   Barnard and co-workers [10] proposed an alternative reaction
mechanism for polyisoprene oxidation in which chain scission of
the Bevilacqua type of peroxylalkoxy radical produces a simple
alkoxy radical that stabilizes itself by abstraction of a hydrogen atom
from a doubly-allylic hydrogen atom to form a secondary alcohol and
a conjugated diene. This oxidation mechanism can be adapted to
PDMB as shown in Scheme C.
   All three of these mechanisms explain 2,5-hexanedione as the main
product from the scission reaction, and this agrees with the experi-
mental results. All of these schemes involve the formation of
hydroxyl radicals which are responsible for the chain propagation.
If all the hydroxyl radicals were involved in the formation of water,
Schemes A and B would call for one molecule of water for each
hexanedione molecule formed, and Scheme C would call for two
water molecules for every hexanedione. In this work only one mole-
cule of water was formed for every eight to nine hexanedione mole-
cules. Most of the hydroxyl radicals thus remain on the oxidized
polymer chain, probably as alcohol groups. Golub and Hsu [9],
from the results of their NMR analysis of oxidized polyisoprene,

SCHEME A.

SCHEME B.

Structure V $\longrightarrow$ $\sim\sim$CH$_2$—C—C—CH$_2$—CH$_2$—C—C=CH$\sim\sim$ + ·OH

（chemical structure V with CH$_3$, CH$_3$, CH$_2$—CH$_2$, CH$_3$, O—O peroxide bridge, CH$_3$）

$\sim\sim$CH$_2$—C—CH$_3$ + CH$_3$—C—CH$_2$—CH$_2$—C—C=CH—CH$_2$—C—C—CH$_2$$\sim\sim\sim$
 O   O

CH$_3$—C—CH$_2$—CH$_2$—C—C=CH—CH—C=C—CH$_2$$\sim\sim$
 O   OH

CH$_3$—C—CH$_2$—CH$_2$—C—C—CH=CH—C=C—CH$_2$$\sim\sim$
 O   OH

O$_2$ ↓

CH$_3$—C—CH$_2$—CH$_2$—C—C—CH=CH—C=C—CH$_2$$\sim\sim$
 O   OH   O
                       O·

↓ abstracts H

CH$_3$—C—CH$_2$—CH$_2$—C—C—CH=CH—C=C—CH$_2$$\sim\sim$
 O   O   O
                 H   O
                     H

eliminates ·OH
scission

↓ eliminates H$_2$O, scission

CH$_3$—C—CH$_2$—CH$_2$—C—CH$_3$ + CH$_3$—C—CH=CH—C=C—CH$_2$$\sim\sim$
 O   O   O
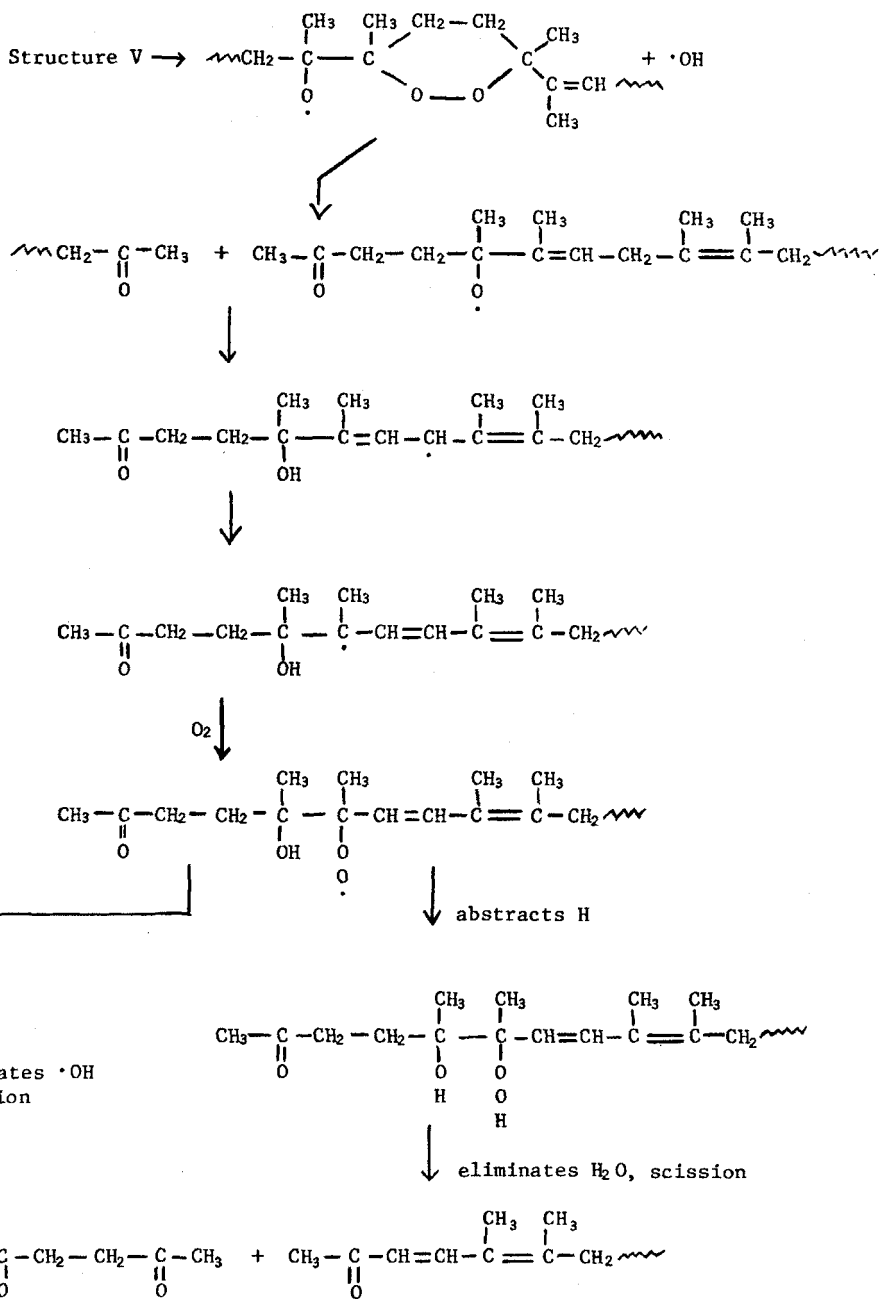
SCHEME C.

concluded that only 20% of the OOH groups expected in the polymer backbone structure, using either the Bolland-Hughes or Bevilacqua structures, were in the form of hydroperoxide groups; the majority were considered to be alcohol groups. A possible explanation for the low yields of water in these experiments could be due to the following reactions that consume hydroxyl radicals without the formation of water:
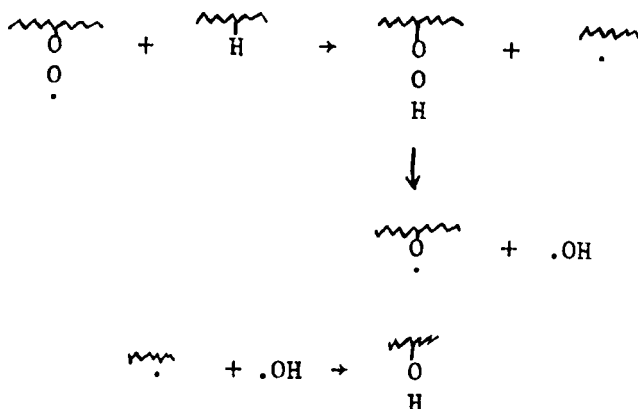
Acetaldehyde and acetic acid were produced in small amounts during the PDMB popcorn oxidation in the relatively constant ratio of 2.7 mol of acid for each mole of aldehyde. Only one two-carbon fragment appeared, however, for every 23 mol of 2,5-hexanedione formed. These data exclude the four-way scission of the Bevilacqua structure as shown in Scheme B as a viable reaction mechanism. Scheme B would require one two-carbon fragment for each 2,5-hexanedione molecule formed.

Comparative data for PIP and PDMB popcorn oxidations are shown in Figs. 1, 4, 5, 6, and 7. PDMB popcorn, on a molar basis, consumes oxygen at a rate over three times that for PIP (Fig. 1). Yields of 2,5-hexanedione are low for PIP (Fig. 4), but twice as much water is formed in PIP oxidation per mole of oxygen consumed (Fig. 7). Both PIP and PDMB popcorn become yellow on extensive oxidation, but PIP yellows much earlier. PIP does not collapse to a viscous gel, but retains its popcornlike structure.

Neither the Bolland-Hughes (Scheme A) nor the Bevilacqua (Scheme B) mechanism can account for the yellowing of the oxidized polymer. Scheme C of Barnard and co-workers, however, can adequately account for this by way of the formation of the highly conjugated terminal ketone.

The experimental data for the PDMB popcorn autoxidation can best be explained using the Barnard (Scheme C) mechanism. Of the two

possible routes for the final scission process, however, the route involving the elimination of a hydroxyl radical followed by scission is favored over the route in which the peroxy radical abstracts an hydrogen atom and water is eliminated prior to scission. Insufficient water is formed for the latter route to be a major contributor to the overall process.

Unfortunately, although this reaction mechanism adequately explains the details of the PDMB popcorn oxidation, it cannot be adapted to the oxidation of PIP.

ACKNOWLEDGMENTS

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