Oxidation of Polyisoprene Popcorn Polymer. VI. Quantitative Determination of Some of the Volatile Reaction Products

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ABSTRACT

The primary products produced during the early stages of
polyisoprene popcorn polymer autoxidation appear to be
water, 2,5-hexanedione, acetaldehyde, and two unknown com-
pounds. Quantitative data are presented for the production
of 2,5-hexanedione and acetic acid. The scission mechanism
undoubtedly involves the formation of acetonyl radicals which
recombine to form 2,5-hexanedione. A scission yield of one
mole of scissions per 53 moles of oxygen was calculated for
the room-temperature oxidation.

INTRODUCTION

Approximately 24 volatile compounds have been detected as products
from the room temperature oxidation of polyisoprene popcorn polymer
(PIP) [1]. Of these, quantitative data have been presented for only the
water yields [2]. A number of these products are, however, the result
of secondary reactions; no carbon dioxide could be detected for

example, during the early stages of the reaction [2]. In this work, quantitative data are reported for the products 2,5-hexanedione and acetic acid.

The diketone, 2,5-hexanedione (acetonyl acetone), was suggested as the primary product in the oxidative scission of natural rubber by Tobolsky and Mercurio [3]:

$$\text{~CH}_2\text{-C=CH} \underset{\text{O—O}}{\overset{\text{CH}_2\text{-C-O}\cdot}{\diagdown}} \text{CH-CH}_2\text{~} \rightarrow$$

with CH$_2$ and CH$_3$ substituents

$$\text{~CH}_2\text{-C=CH-C=O} + \text{CH}_3\text{-C-CH}_2\cdot + \text{HC-CH}_2\text{~}$$

$$2\text{CH}_3\text{-C-CH}_2\cdot \rightarrow \text{CH}_3\text{-C-CH}_2\text{-CH}_2\text{-C-CH}_3$$

2,5-Hexanedione was also found to be a product from the oxidation of cis-1,4-polyisoprene by Bevilacqua and Norling [4]. At an oxidation temperature of 150 to 180°C, they reported yields that amounted to 5 to 10% of the levulinaldehyde produced. These authors also reported 2,5-hexanedione as an oxidation product from ethylene-propylene copolymers. They proposed a scheme for the latter reaction involved the following steps:

$$\text{~CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{~} \rightarrow \text{~CH}_2\text{-C-CH}_2\text{-C-CH}_2\text{~} \rightarrow$$

$$\text{~CH}_2\cdot + \text{CH}_3\text{-C-CH}_2\cdot + \text{CH}_3\text{-C-CH}_2\text{~}$$

$$2\text{CH}_3\text{-C-CH}_2\cdot \rightarrow \text{CH}_3\text{-C-CH}_2\text{-CH}_2\text{-C-CH}_3$$

In a previous paper of this series [1], 2,5-hexanedione was reported as one of the products from the room temperature oxidation of PIP, but

no levulinaldehyde was identified. It has since been found that when PIP is carefully purified by the removal of all the volatile dimeric species [2], the 2,5-hexanedione becomes a primary volatile product of the oxidation reaction, second only to water in amount. The tentative reaction mechanism previously discussed can now be reviewed in the light of these findings.

Acetic acid has been recognized by most workers in this field as one of the major volatile oxidation products from polyisoprenes [5]. The chromatographs presented by Bevilacqua [6] indicate that acetic acid is the major volatile product next to water. No quantitative data, however, has been presented for the production of acetic acid during the early stages of the autoxidation.

EXPERIMENTAL

The experimental procedure has been described in detail [2]. The results presented in this paper were obtained from the same polymer samples used for the previously reported water-yield experiments. Third generation PIP seeds were used and all handling of the polymer samples was done in the inert atmosphere of a glove box that was continuously flushed with dry nitrogen. Volatile impurities (monomer and dimers) were removed by flushing the PIP with a stream of dry helium for periods from 316 to 390 hr.

All oxidations were at room temperature using an oxygen flow of 50 ml/min. Each 3 or 4 hr oxidation period was followed by a 20 to 21 hr helium flush to remove volatile reaction products.

Chromatographic analyses were made on a Hewlett-Packard model 7620A research chromatograph using a Poropak QS column and a temperature program as previously described [2]. Peak areas were integrated by means of a disk integrator and compared to areas obtained from standard samples.

Volatile reaction products were collected at Dry-Ice temperature and the collection traps were rinsed with four 50-μl aliquots of absolute ethanol. Ten microliter portions were used for each analysis, and the average result obtained from 3 or 4 analyses was used for each point graphed.

Positive identifications of 2,5-hexanedione and acetic acid were obtained by mass spectroscopy and, in the case of hexanedione, also by NMR.

EXPERIMENTAL RESULTS

The rate of oxygen uptake by PIP during the first 25 hr of oxidation at room temperature is shown in Fig. 1. No induction period was noted. The induction period and initial loss of sample weight shown on previously reported oxidation curves [7] were absent due to the
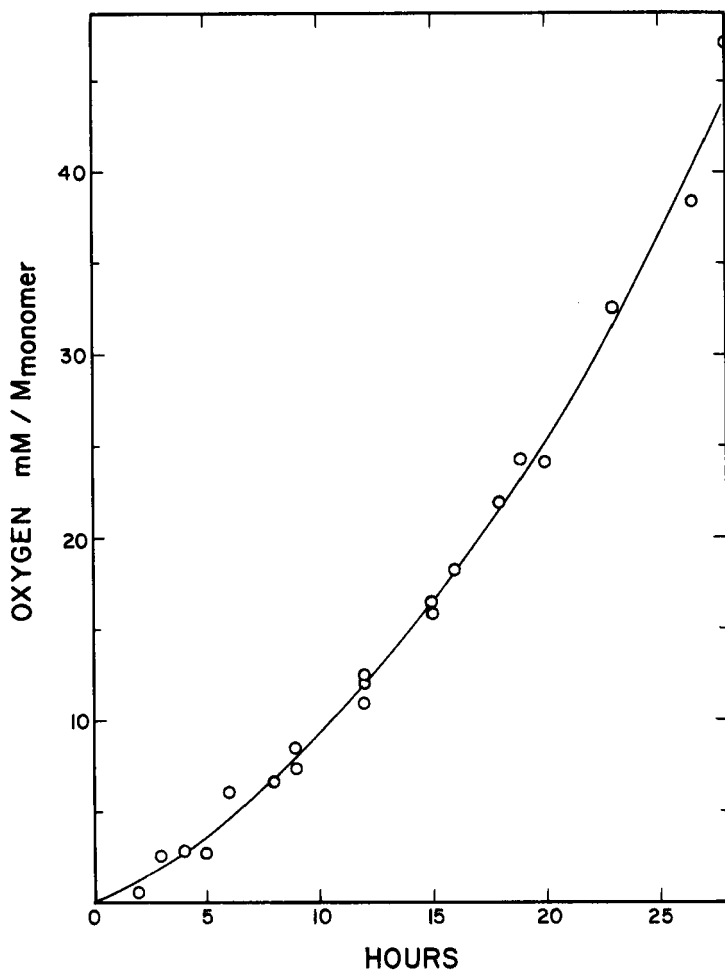
FIG. 1. Oxidation rate for polyisoprene popcorn polymer.

removal of all dimeric species by the extended helium flushing prior
to the oxidation.

　　Chromatographs for the volatile products obtained from the oxida-
tion of PIP after various time intervals are shown in Figs. 2, 3, and 4.
The numbers below the curves indicate changes in the sensitivity of
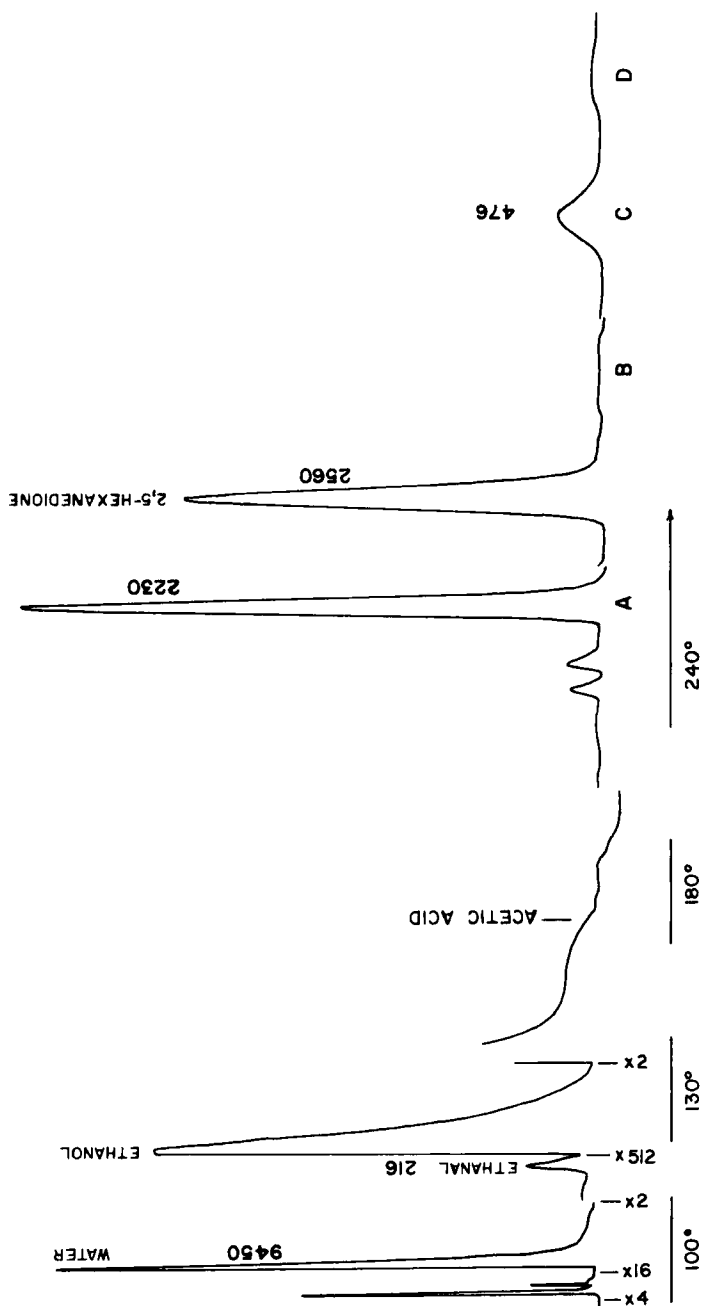the recording, and the relative peak-area integrations are shown for

FIG. 2. Chromatogram of volatile products collected during the first 2 hr of polyisoprene popcorn polymer autoxidation.
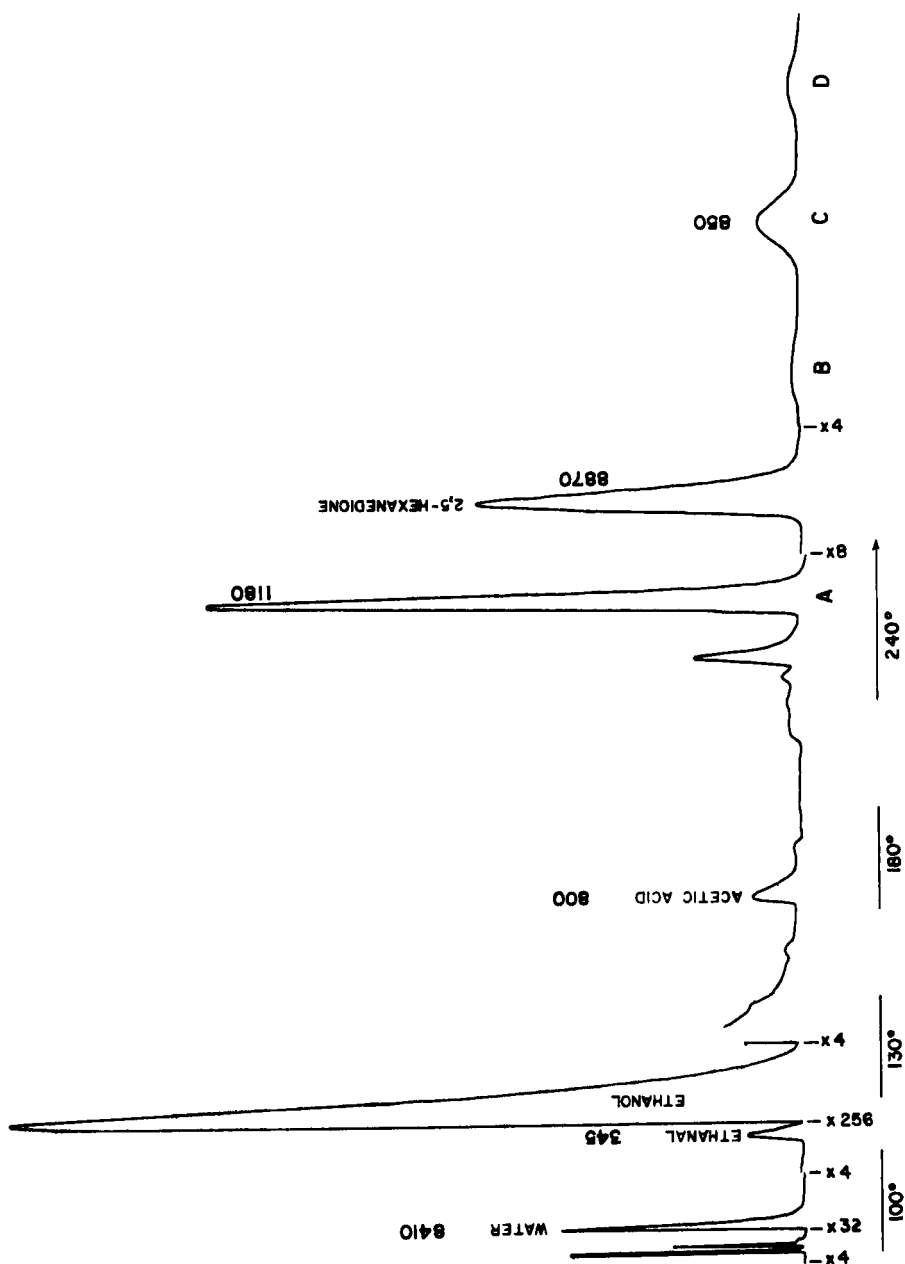
FIG. 3. Chromatogram of volatile products collected during the 9 to 12-hr period of polyisoprene popcorn polymer autoxidation.
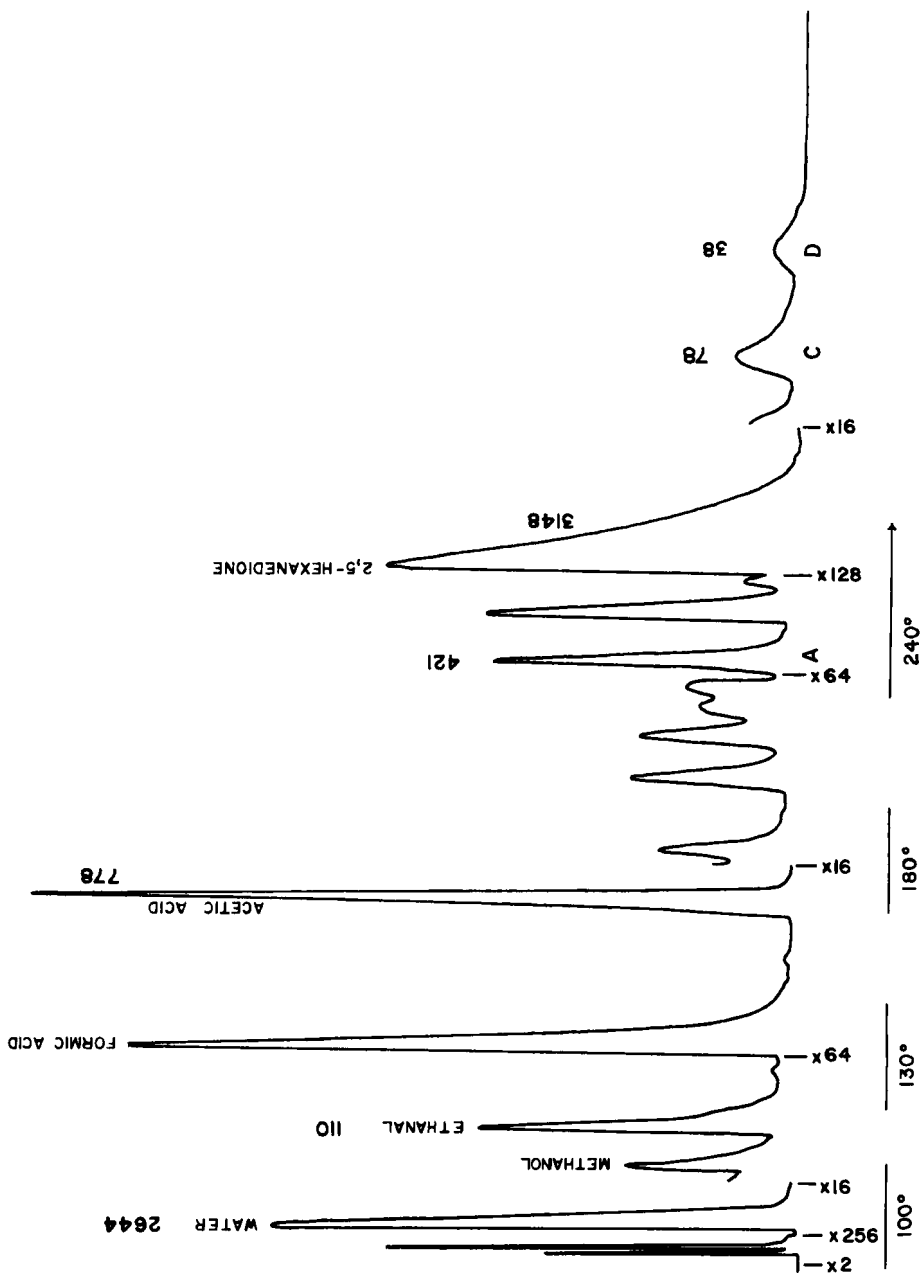
FIG. 4. Chromatogram of volatile products collected during the 34 to 40–hr period of polyisoprene popcorn polymer autoxidation.

the primary products. The large ethanol peaks on Figs. 2 and 3 are due to the ethanol used to rinse the trap and collect the small samples; a neat sample was used for Fig. 4 data.

Figure 2 shows the distribution of the volatile products collected during the first 2 hr of PIP oxidation. The primary products, in the order of their relative peak areas, are: water, 2,5-hexanedione, Compound A, Compound C, and acetaldehyde. There is no positive evidence for acetic acid, and any formic acid present would be masked by the large ethanol peak.

Figure 3 gives the chromatograph for the product collected during the 9 to 12 hr oxidation period. The changes noted are the appearance of a significant amount of acetic acid and a decrease in the amount of Compound A relative to the 2,5-hexanedione.

The chromatograph for the products collected during the 34 to 40 hr period is shown in Fig. 4. At this point in the oxidation, sufficient material was collected so that it was no longer necessary to use the ethanol solvent. Formic acid and acetic acid are now prominent products. Methanol and numerous other secondary products are also present. Compound A has continued to decline in amount relative to 2,5-hexanedione and is no longer the third major product. A new peak, between Compound A and 2,5-hexanedione, now becomes as important as Peak A.

Of all the unidentified compounds, Peak A, the one that is eluted prior to 2,5-hexanedione on the 0 to 2 hr oxidation sample, is of greatest interest. It appears to be a primary product of the reaction, but the amounts produced diminish as the reaction proceeds. All attempts to obtain a positive identification have failed. The samples of this compound collected during the later stages of the reaction, when sufficient quantity can be obtained for analyses, have apparently been contaminated with other compounds. Its mass spectrum, however, appears to indicate a methyl ketone with a parent peak of $m/e =$ 110. The following prominent m/e peaks were also present: 43, 44, 55, 70, 81, 82, and 95. A comparison of the elution time for Compound A with those of known samples has failed to aid in its identification. No levulinaldehyde was available for a comparison of elution times, but the 110 parent peak noted for Compound A would exclude levulinaldehyde as a possibility.

The millimoles of 2,5-hexanedione produced per mole of original monomer unit are plotted as a function of time in Fig. 5, and as a function of the millimoles of oxygen reacted per mole of initial monomer unit in Fig. 6. The production of 2,5-hexanedione is a linear function of the amount of oxygen reacted and amounts to 0.00938 mole of 2,5-hexanedione per mole of oxygen reacted; that is, approximately 1 mole of 2,5-hexanedione for every 100 moles of reacted oxygen.

Data for acetic acid are shown in Figs. 7 and 8. Acetic acid does not appear as a product until after the first 3 or 4 hr of oxidation.
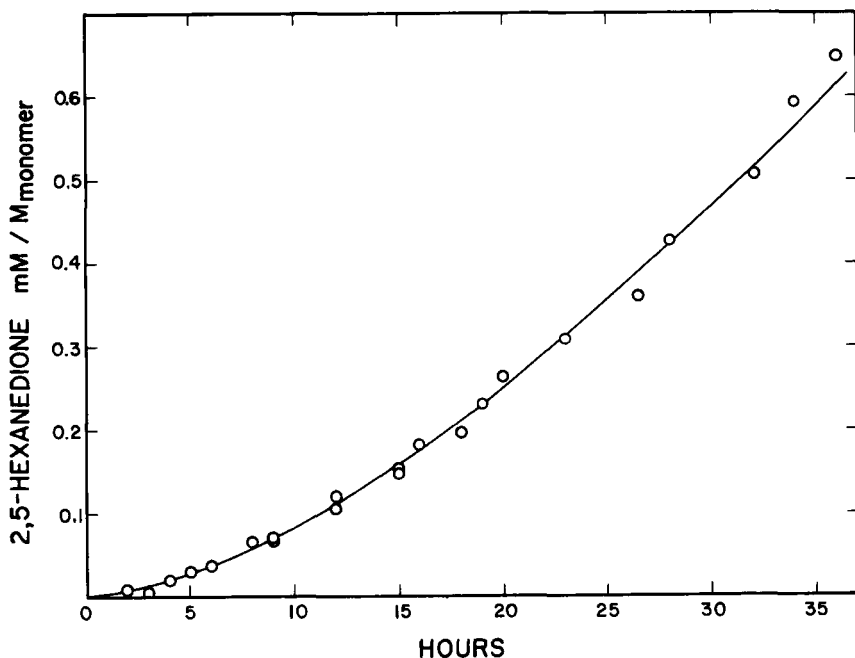
FIG. 5. Rate of 2,5-hexanedione production during the early
stages of polyisoprene popcorn polymer autoxidation.

The rate of its production as a function of the amount of oxygen re-
acted, Fig. 8, shows that its production appears to be quite linear
for a short period, but then increases rapidly.

   The data of Fig. 9 present some approximate calculations for the
unknown Products A and C. The A curve was obtained by assuming
a molecular mass of 110 and a thermal conductivity equal to that of
pentanedione. For the C curve, a molecular mass of 130 was
assumed and a thermal conductivity equal to that of hexanedione.
Product A appears to be produced at a rate which is approximately
linear with time. Product C, however, appears to increase only
very slowly in amount after the first 10 hr of the oxidation.

DISCUSSION AND CONCLUSIONS

   A list of the volatile products obtained from the oxidation of
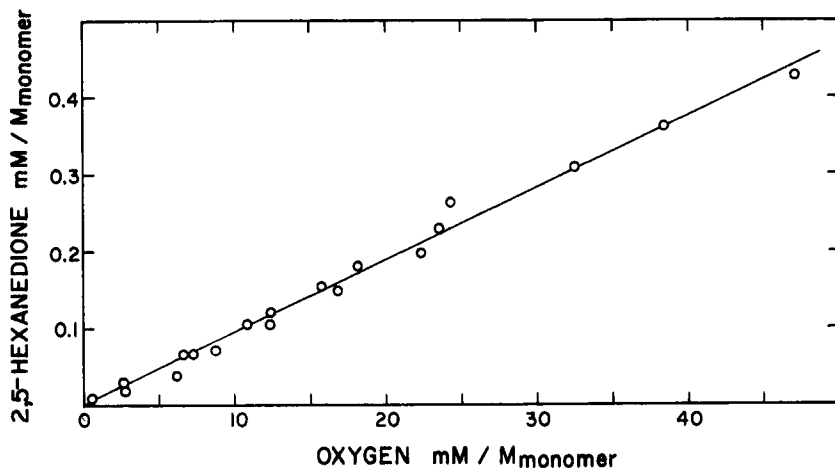natural rubber was presented by Bevilacqua [6]. Using primarily a

FIG. 6. Rate of 2,5-hexanedione formation as a function of oxygen consumed during the early stages of polyisoprene popcorn polymer autoxidation.
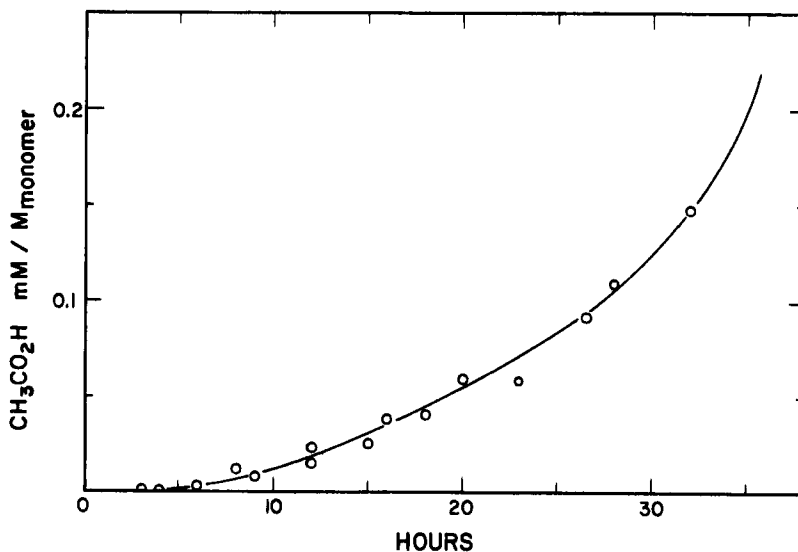
FIG. 7. Rate of acetic acid production during the early stages of polyisoprene popcorn polymer autoxidation.
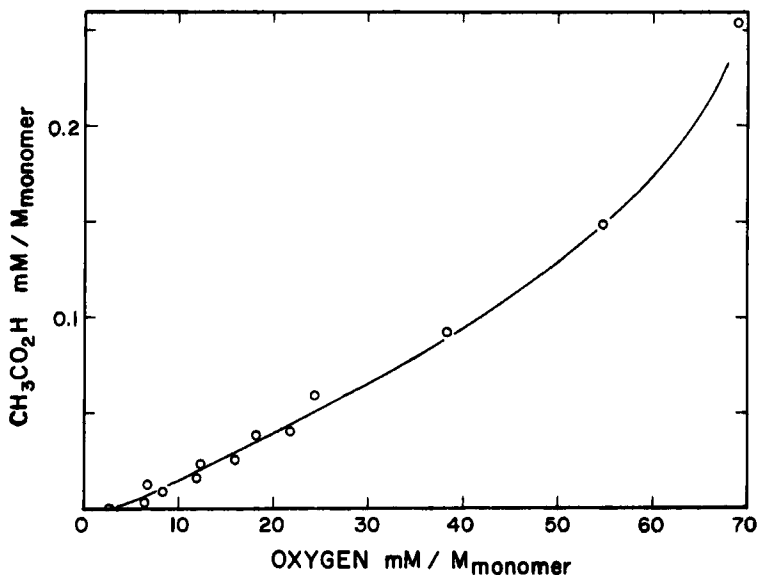
FIG. 8. Rate of acetic acid formation as a function of oxygen consumed during the early stages of polyisoprene popcorn polymer autoxidation.

Pluronic P84 column, he identified over 20 volatile compounds resulting from the oxidation of a peroxide-vulcanized rubber. Hexanedione was found to be a product; however, the compounds water, acetic acid, formic acid, acetaldehyde, and a compound believed to be levulinaldehyde were present in greater amounts. He could not determine from his work which of the products were primarily and which were the result of secondary reactions. It is also not possible to directly compare Bevilacqua's results with those obtained in this work for PIP because he used a peroxide-vulcanized rubber that was already partially oxidized and his studies were made at a higher temperature.

One of the purposes of the present study was to identify those compounds that appear to be primary scission fragments and to distinguish them from secondary products resulting from the oxidation of already-produced oxidation products. The products which appear to be primary products from the oxidation of PIP are: water, 2,5-hexanedione, Compound A, acetaldehyde, Compound C, and traces of several other compounds (Fig. 2). Products A and C are as yet unidentified. Compound A appears to be a methyl ketone with a molecular mass of 110; it is not, however, 2-acetylfuran. Compound C, having a molecular
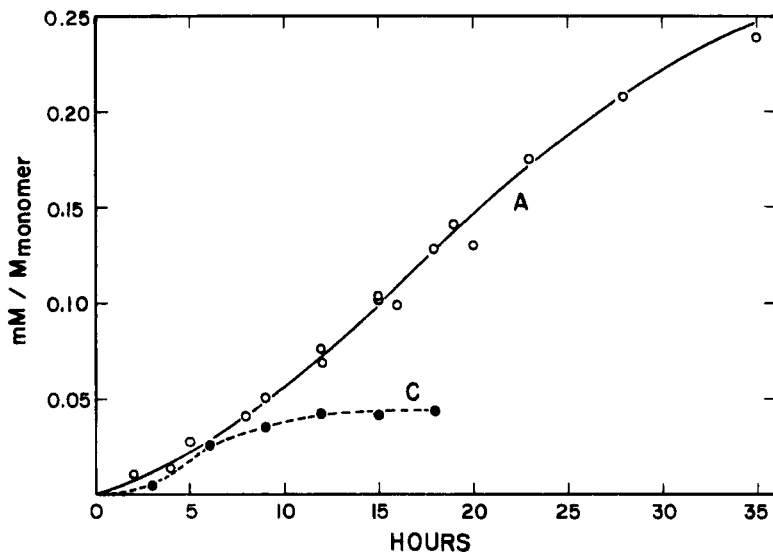
FIG. 9. Rate of formation of Compounds A and C (estimated).

mass greater than 2,5-hexanedione, is not one of the isoprene dimers and is not one of the lactones identified by Bevilacque.

Bevilacqua [9] reported the total volatile methyl ketone (CH_3CO) yields from the 120 to $140°C$ oxidation of raw rubber, a filled peroxide vulcanizate, and a sulfenamide gum vulcanizate. A linear relationship was obtained when the yields were plotted as a function of the amount of oxygen reacted. Approximately 2.8 moles of (CH_3CO) were produced for every 100 moles of oxygen reacted. These results compare favorably with the yields of 2,5-hexanedione found from PIP oxidation; 0.94 moles of 2,5-hexanedione for every 100 moles of oxygen reacted (Fig. 6). Since hexanedione contains two (CH_3CO)'s per molecule, the total volatile methyl ketone yield equals 1.88 moles/100 moles oxygen reacted. The lower result obtained for PIP is expected since other methyl ketones, such as Compound A, are also present.

Many values are reported in the literature for the scission efficiency in the oxidation of rubbers [10-16]. Most workers agree that the scission efficiency increases as the oxidation progresses. A plot of the results of numerous investigators [10] gives values ranging from approximately 40 moles oxygen per mole scissions at $30°C$ to approximately 5 moles of oxygen per mole of scissions at $140°C$. Farmer and Sundralingham [17], however, in their photooxidation experiments, found values ranging from 30 to 70 moles of oxygen/mole

scissions; the higher value being obtained at the higher temperatures. An estimate for the chain-scission efficiency for PIP can be obtained from the quantitative hexanedione yield data. If one assumes that the hexanedione is produced via acetonyl radicals, one acetonyl radical per scission, then there is a scission rate of 1.88 moles of scissions per 100 moles of oxygen reacted, or 53 moles of oxygen per mole of scissions at room temperature. This result agrees favorably with the data of Bevilacqua [9]. Using his value of 2.8 moles of methyl ketone produced for every 100 moles of oxygen reacted, one calculates a scission yield of 36 moles of oxygen per mole of scissions at 120 to 140°. The higher value obtained for PIP would be expected due to the lower temperature of oxidation and the fact that the PIP polymer had not been previously exposed to oxygen.

It is doubtful whether acetic acid is a primary product from the oxidation of PIP. Very small amounts may be present in the volatile products collected after the first 2 hr of room temperature oxidation, but it would be undetectable in this work due to the tailing of the ethanol solvent peak on the chromatograph (Fig. 2). Acetaldehyde, however, does appear to be a primary product, and acetic acid definitely makes its appearance after the first 4 or 5 hr of oxidation (Fig. 3). The rate of acetic acid production plotted as a function of the amount of oxygen reacted is quite linear during the early stages of the reaction, but increases after approximately 40 mmoles of oxygen have reacted per mole of monomer initially present. The acetic acid is undoubtedly a secondary product formed from the further oxidation of acetaldehyde. Sufficient data were not obtained in this work to construct a plot of total C_2 yield (acetic acid plus acetaldehyde) as a function of oxygen consumed, but it is predicted that this curve would be linear. The production of acetaldehyde relative to the major products water and hexanedione decreases with time of oxidation while that of acetic acid increases.

Early reported data on the oxidation of latex at low temperatures showed that each scission led to one molecule of acetic acid, one of formic acid, and approximately three of carbon dioxide. Based on this evidence, and the fact that the compound levulinaldehyde can be oxidized to acetic acid and carbon dioxide in dilute aqueous ammonia, many workers have concluded that the primary scission fragments are levulinaldehyde and a one-carbon fragment, formic acid. Numerous oxidation mechanisms have been based on these assumptions. They do not apply, however, to the oxidation of PIP. No evidence has been obtained for levulinaldehyde as a primary product, carbon dioxide is not a primary product, and the major products are 2,5-hexanedione and water. No evidence for the early production of formic acid could be obtained in this work due to the masking of any formic acid peak on the chromatographs because of the ethanol solvent present. A series of oxidations in which another, higher-boiling solvent is used, so that any early production of formic

acid can be noted, would furnish valuable information on this point.

2,5-Hexanedione can be readily accounted for as a primary product from the oxidation of PIP if one assumes the intermediate formation of acetonyl radicals as primary scission products. These acetonyl radicals could originate via the Tobolsky-Mercurio mechanism mentioned in the introduction of this paper [3], or by means of the reaction sequence previously proposed for PIP oxidation [1].

$$\sim CH_2 - \underset{\underset{O}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{O-O}{}}{CH} - CH - CH_2 - \underset{\underset{O}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH - CH_2 - \underset{\underset{\underset{\underset{H}{|}}{O}}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH \sim \ \rightleftharpoons$$

$$\sim CH_2 - \underset{\underset{\underset{H}{|}}{O}}{\overset{\overset{CH_3}{|}}{C}} - C = CH - CH_2 - \underset{\underset{O-O}{}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH - CH_2 - \underset{\underset{\underset{\underset{H}{|}}{O}}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH \sim \ \rightarrow$$

$$\sim CH_2 - \overset{CH_3}{C} \cdots CH - CH + CH_2 - C + CH = CH - CH_2 - \underset{\underset{\underset{\underset{H}{|}}{O}}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH \sim \ \rightarrow$$

$$CH_2 - CO - CH_3$$

The Tobolsky-Mercurio mechanism does not account adequately for the production of water as the primary product. The alternative mechanism above, however, does account for both the water and the 2,5-hexanedione, but there is a residual fragment $\cdot OCH - \overset{\cdot}{C}HOO \cdot$. It

was originally believed that this fragment resulted in formaldehyde and carbon dioxide, but the absence of carbon dioxide as a product from pure PIP excludes this possibility. At this time, one can only conclude that this fragment is responsible for the yields of acetaldehyde and possibly, in combination with acetonyl radicals, Compounds A and C.

The recently proposed alternative oxidation scheme for polyisoprenes presented by Barnard et al. [15] is not applicalbe since it is based on levulinaldehyde as a primary scission product. The present work is in substantial agreement with Shelton [8], who states that it is possible that no single structure is adequate to account for the observed products and a number of mechanisms may be involved.

REFERENCES

[1]   G. H. Miller and Shih-chen Lu, J. Macromol. Sci.—Chem., A7(3), 753 (1973).

[2]   G. H. Miller, J. Macromol. Sci.—Chem., A8, 281 (1974).

[3]   A. V. Tobolsky and A. Mercurio, J. Amer. Chem. Soc., 81, 5535 (1959).

[4]   E. M. Bevilacqua and P. M. Norling, Science, 147, 289 (1965).

[5]   E. M. Bevilacqua, E. S. English, J. S. Gall, and P. M. Norling, J. Appl. Polym. Sci., 8, 1029 (1964).

[6]   E. M. Bevilacqua, in Thermal Stability of Polymers, Vol. 1 (Robert T. Conley, ed.), Dekker, New York, 1970, p. 211.

[7]   G. H. Miller and H. Leung, J. Macromol. Sci.—Chem., A4(8), 1705 (1970).

[8]   J. R. Shelton, Rubber Chem. Technol., 45, 359 (1972).

[9]   Ref. 6, p. 208.

[10] E. M. Bevilacqua, Rubber Chem. Technol., 30, 667 (1957).

[11] A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, J. Amer. Chem. Soc., 72, 1942 (1950).

[12] M. M. Horikx, J. Polym. Sci., 19, 445 (1956).

[13] E. M. Bevilacque, J. Amer. Chem. Soc., 77, 5394 (1955).

[14] E. M. Bevilacqua, J. Org. Chem., 21, 369 (1956).

[15] D. Barnard, M. E. Cain, J. I. Cunneen, and T. H. Houseman, Rubber Chem. Technol., 45, 381 (1972).

[16] C. L. M. Bell and R. F. Tiller, J. Appl. Polym. Sci., 11, 1289 (1967).

[17] E. H. Farmer and A. Sundralingham, J. Chem. Soc., 1943, 125.