Thermal Oxidation of Polypropylene in the Temperature Range of 120–280°C*

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Synopsis

Thermal oxidation of isotactic polypropylene films at 120–280°C in air was studied. Separation and identification of the volatiles formed was carried out by gas chromatography–mass spectrometry. Sixteen products were tentatively identified for the first time. Altogether, 50 compounds representing hydrocarbons, ethers, alcohols, aldehydes, ketones, and acids are reported. Oxygen deficiency is manifested in diffusion-limited products of olefines, dienes, and aromatic compounds. The relative amounts of acetaldehyde and acetone are almost temperature independent in the range of 120–280°C. This indicates a similarity of oxidative degradation of the polymer in a broad temperature range. Addition of an antioxidant to the polymer depresses the evolution of the main volatiles by 9–10 times at 280°C. The relative amounts of the volatiles formed are, nevertheless, the same as for the polymer without an antioxidant. The mechanism of formation of the degradation products is discussed.

INTRODUCTION

Among the thermoplastics produced in the world during the last decade, polypropylene (PP) has shown the highest increase in the rate of growth.[1] Such a rapid industrial development of PP has been achieved by a combination of outstanding product properties and convenient processes capable of undergoing more advanced simplification. One of the major disadvantages of PP is, however, that without stabilizers the polymer is highly susceptible to photo- and thermal oxidation.

Numerous studies have been conducted on the oxidation of PP below the melting point of the polymer,[2–15] which have illuminated the main features of the process. The processing of PP is carried out, however, at temperatures up to 310°C, i.e., at temperatures which are considerably higher than those which have been studied. Very few studies have been devoted to oxidation of PP at these temperatures.[16–18] Chien and Kiang,[17] who studied the oxidative pyrolysis of PP at 240–289°C, have shown that the observed rate constants and activation energies may be calculated from kinetic parameters measured earlier for autoxidation of PP at 71–140°C. Good agreement was obtained implying a similarity of oxidative degradation of PP spanning a large temperature range. In addition, there is some experimental evidence that the relative amounts of the main volatile products formed during oxidation of PP at 280°C are close to those

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obtained at 130°C.[18]   Therefore, it seemed interesting to follow more closely
the oxidation of PP in a broad temperature range, between 120°C and 280°C.
Another objective of this work was to study the effect of antioxidants on the
oxidation of PP at high temperatures.

In this work, the thermal oxidation products have mainly been studied by gas
chromatography–mass spectrometry (GC/MS).

EXPERIMENTAL

Materials

Shell Polypropylene KM 6100, for general purposes, molding quality, and
without additives was used.   This is a crystalline, isotactic polymer having the
following characteritics: density 0.905 g/cm^3; melt index 3.5 (2.16 kg at 230°C).
Polymer films (50 μm) were molded at 210–220°C for 60–90 s.

The following antioxidants were used: Irganox 1010 which is a pentaery-
thrityl-tetrakis [3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], melting point
110–125°C, and Irganox B561, which is a blend of Irganox 1010 (one part by
weight) and Irgafos 168 (4 parts by weight).   Irgafos 168 is an organophosphite,
melting point 180–185°C.   These antioxidants are commercial products supplied
by Ciba-Geigy.   The antioxidants [1.0 % (w/w) of the polymer] were blended with
PP in the following way.   The solution of antioxidants in acetone or chloroform
was evenly dispersed by a syringe over two symmetrically cut films of PP.   After
the solvent had evaporated, the films were placed together and molded to form
a new film.   This film was cut into small pieces and molded again; this operation
was repeated three times.

Methods

The procedure of oxidation was performed in a reaction tube (i.d. 22 mm) with
an air flowrate of 34 ml/min (at 22°C).[18]   The GC/MS system used was an
modified LKB 9000,[19] interfaced to an INCOS 2400 Data System.

Separation of the volatile products formed on thermal oxidation of PP was
carried out on silanized glass columns (2.0 m × 1.8 mm i.d.) packed with either
6% OS-138 on Tenax GC, 80/100 mesh, or 0.1% SP 1000 on Carbopack C, 80/100
mesh.   The chromatograms presented below are either total ion current (TIC)
chromatograms or those obtained by single ion monitoring (SIM).

Infrared spectra of the polymer films were obtained using a Perkin-Elmer 297
Spectrometer.   Weight measurements of the polymer films before and after
oxidation were performed on a Cahn electrobalance, Model 4100.

RESULTS AND DISCUSSION

Thermal oxidation of PP results in formation of a complex mixture of volatile
products.   Apart from water and carbon oxides, 47 organic compounds have been
identified (see Table I).   Among the products which are given in Table I, 16
compounds have been identified for the first time in this connection.   Charac-
terization of these substances was based mainly on mass spectral data.   Chro-
matograms illustrating the separation of the products formed on oxidation of

TABLE I
Products of Polypropylene Thermooxidation

Compound	Peak no. on column OS-138 Figs. 1 and 2	Carbopack C Fig. 3	Identification GC	MS
Hydrocarbons				
Ethene			a	b
Ethane			a	b
Propene			a	b
Propane			a	b
Isobutene				c
Butane		1	a	b
Isobutane		2		c
Pentadiene[d]		17		c
2-Methyl-1-pentene	10			c
2,4-Dimethyl-1-pentene[d]		24		c
5-Methyl-1-hepten[d]		38		c
Dimethylbenzene[d,e]	19	42		c
Alcohols				
Methanol	4		a	b
Ethanol	7		a	b
2-Methyl-2-propen-1-ol	14	14	a	b
Ethers				
2-Methylfuran[d]		16		c
2,5-Dimethylfuran	17		a	b
Aldehydes				
Formaldehyde	2		a	b
Acetaldehyde	6	5	a	b
Acrolein	9		a	b
Propanal	10	9	a	b
Methacrolein	12	11	a	b
2-Methylpropanal	11	7		c
Butanal		9		c
2-Vinyl-crotonaldehyde[d]		28		c
3-Methylpentanal[d]	16			c
3-Methylhexanal[d]	18			c
Octanal[d,f]	20			c
Nonanal[d,f]	23			c
Decanal[d,f]	25			c
Ketones				
Ethenone[d]	1			c
Acetone	9	8	a	b
3-Buten-2-one		12		c
2-Butanone	13		a	b
1-Hydroxy-2-propanone	16	15	14	a	b
1-Cyclopropylethanone	18		a	b
3-Methyl-3-buten-2-one[d]		20		c
3-Penten 2-one[d]		26		c
2-Pentanone	15	19	a	b
2,3-Butanedione		13		c

(*continued*)

[a] According to retention time.
[b] According to mass spectra of individual compounds.
[c] According to mass spectra compared with those obtained by a computerized library search.
[d] Compounds which have been reported probably for the first time.
[e] Probably 1,2-dimethylbenzene.
[f] Probably 3,5-dimethyl-substituted aldehyde.

TABLE I   (*Continued from the previous page.*)

Compound	OS-138 Figs. 1 and 2		Carbopack C Fig. 3	Identification GC	MS
1-Cyclopropyl-2-propanone[d]			22		c
2,4-Pentanedione	20	17	29	a	b
4-Methyl-2-pentanone			27		c
4-Methyl-2-heptanone	23		39		c
Acids					
Formic acid	8			a	b
Acetic acid	11	15		a	b
Propanic acid[d]	14			a	b

PP at different temperatures are shown in Figures 1, 2, and 3. The most abundant products formed during oxidation of PP at 280°C were acetaldehyde, formaldehyde, acetone, methacrolein, and acetic acid followed by 1-cyclopropylethanone, 2,4-pentanedione, 4-methyl-2-pentanone, and 4-methyl-2-heptanone. During oxidation of PP at 120°C for 40 min, the most abundant products detected were aldehydes: probably 3,5-substituted dimethylhexanal, dimethylheptanal, and dimethyloctanal.

Thin films were used and ample air flow was maintained during the experiments. Despite this, the oxidative degradation is limited by oxygen diffusion as indicated by the formation of hydrocarbons. The hydrocarbons constitute,
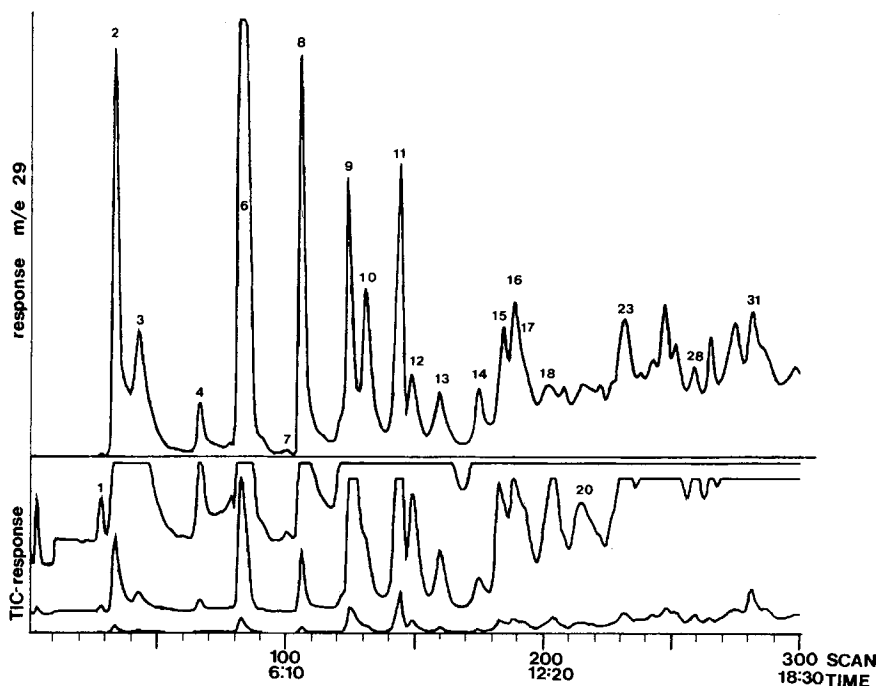

Fig. 1. Gas chromatographic separation of the products of PP oxidation at 280°C on OS-138 column. For identity of certain peaks see Table I.
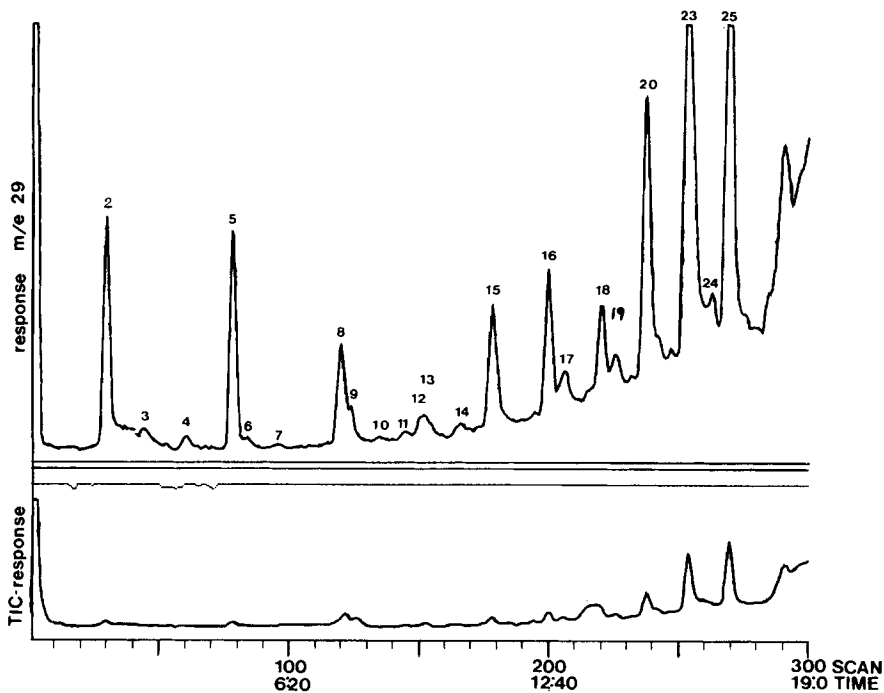
Fig. 2. Gas chromatographic separation of the products of PP oxidation at 120°C on OS-138 column. For identity of certain peaks see Table I.
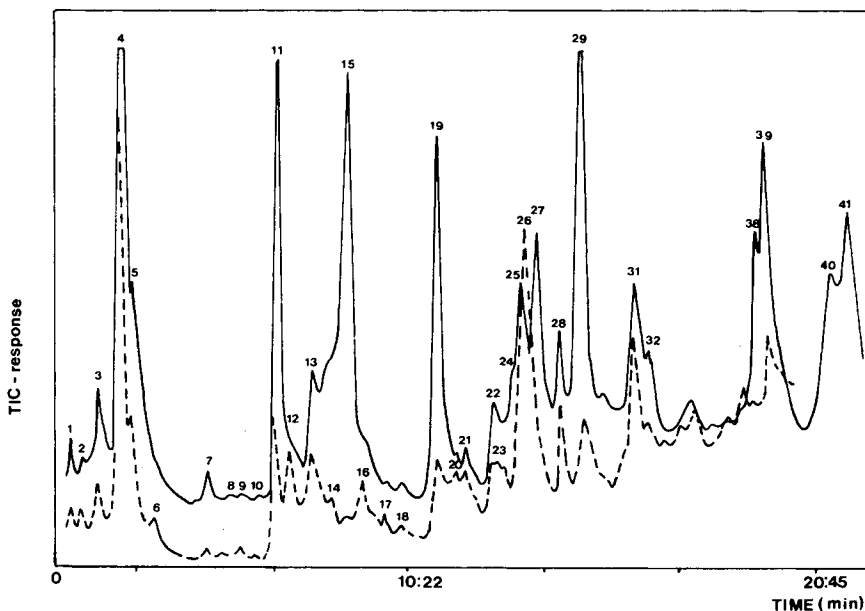

Fig. 3. Gas chromatographic separation of the products of PP oxidation on Carbopack C. For identity of certain peaks see Table I: (a) 1 mg of PP, 279°C, 2 min (——); (b) 18 mg of PP, 148°C, 35 min (- - -).
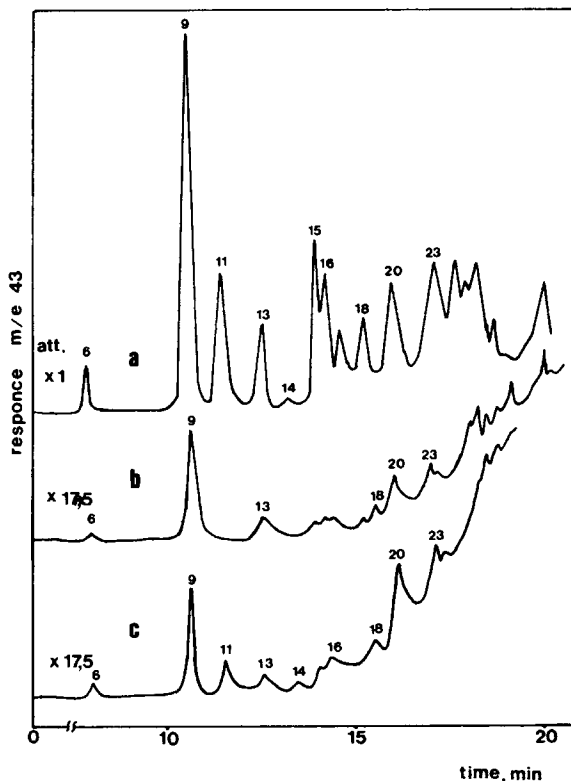
Fig. 4. Gas chromatography analysis of products formed on the oxidation of PP on OS-138 column. The peak numbering is made according to Figure 1 (see Table I):   (a) 0.7 mg of PP, 282°C, 2 min in air; (b) 14 mg of PP, 120°C, 40 min in air; (c) decomposition of PP hydroperoxide formed in case (b); 180°C, 6 min in helium.

however, only a minor fraction of the volatile organic products found.   Oxygen deficiency has also been observed during pyrolysis of PP at 240–289°C.[17]

A comparison of the gas chromatograms of the volatiles formed on oxidation of PP at 280°C, at 120°C and on the thermal decomposition of the preoxidized polymer is shown in Figure 4.

On the basis of these experiments some important observations can be made. For the first, the main difference between low-temperature oxidation (120°C) and high-temperature oxidation (280°C) is that at low temperature rather small amounts of short chain volatiles and relatively large amounts of long chain volatiles are formed, at the high temperature the opposite is true (compare Figs. 1 and 2).   For the second, the nature of at least the most volatile products up to 4-methyl-2-heptanone is essentially the same in all cases, except for acetic acid. This product was found both on oxidation of PP at 280°C, and on the decomposition of the pre-oxidized polymer.   However, it was not detected on oxidation of PP at 120°C.   For the third, the main oxidation products formed on oxidation of PP at 120°C are dimethyl-substituted hexanal, heptanal, and octanal.   These aldehydes were not detected on oxidation of PP at 280°C.   In this case, the corresponding peaks might have been heavily overlapped by other oxidation products.   The relative amounts of the main volatiles such as water, formalde-

TABLE II
Relative Amounts of Oxidation Products of PP

Compound	Relative amounts at different temperatures (°C)					
	120	125[2]	220[18]	280[18]	280[a]	Photolysis of PP hydroperoxide at 35°C[20]
Water	—	100	100	100	—	100
Formaldehyde	—	1.8	0.59	0.76	0.61	—
Acetaldehyde	1.0	1.0	0.92	0.98	1.0	0.71
Acetone	0.42	3.0	0.44	0.40	0.30	2.5
Acetic acid	—	—	0.36	0.40	—	1.4
Methacrolein	—	—	0.26	0.24	—	—
2-Pentanone	—	—	0.05	0.06	—	—

[a] PP with Irganox B561.

hyde, acetaldehyde, acetic acid, etc., formed on oxidation of PP at vastly different experimental conditions are given in Table II. The experimental results obtained in this study are compared with the results of PP oxidation at 120°–140°C[2] and with the results obtained by photolysis of PP hydroperoxide.[20] It can be seen that the relative amounts of the volatiles formed are almost independent of the temperature of oxidation. This conclusion applies both to the neat PP samples and to polymer samples containing 1% (w/w) of antioxidant.

Effect of Antioxidants

IR spectra of the polymer films oxidized at 250°C and 280°C during 2–3 min are shown in Figure 5. It can be seen that the neat polymer sample shows a
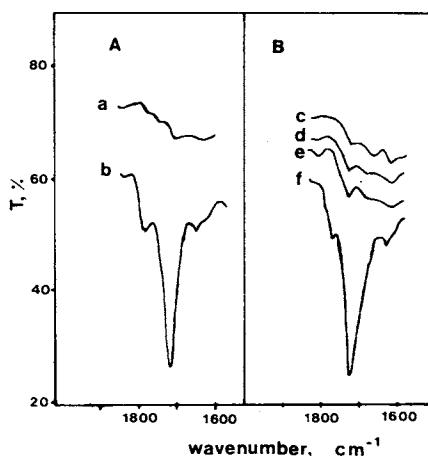

Fig. 5. Infrared spectra of PP in the range 1600–1800 cm^{-1}: (A) PP without antioxidant: (a) the original film; (b) after 2 min of oxidation at 250°C. (B) PP with 1% (w/w) of Irganox B561: (c) the original film; (d) after 2 min of oxidation at 250°C; (e) after 2 min of oxidation at 280°C; (f) after 3 min of oxidation at 280°C.
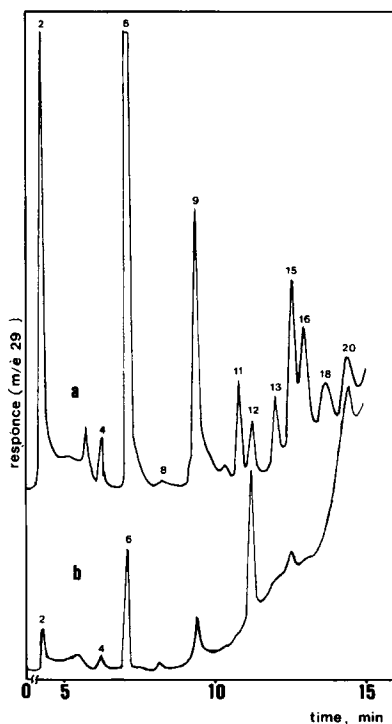
Fig. 6. Gas chromatographic separation of products formed on the oxidation of PP at 280°C, on OS-138 column. The peak numbering is made according to Figure 1 (see Table I): (a) 0.38 mg PP; (b) 0.30 mg of PP with 1% (w/w) of Irganox B561.

strong carbonyl absorption after 2 min of oxidation at 250°C. For a polymer sample containing an antioxidant (Irganox B561) no carbonyl absorption can be observed even after 2 min of oxidation at 280°C. A rather strong absorption band appears, however, after 3 min of oxidation at 280°C. Weight measurements of the polymer samples before and after oxidation at 280°C (2 min) have shown that the neat polymer samples lose about 10–15% (w/w), while the samples containing Irganox B561 lose about 1–2% (w/w). The corresponding values at 250°C (2 min) for both sample types are almost the same, about 1% (w/w). In Figure 6 two typical gas chromatograms are shown, one emanating from thermal oxidation products from a neat polymer sample (a) and the other from oxidation products (b) from a polymer sample containing an antioxidant (Irganox B561). It can be seen that there is a substantial lower emission of volatile products from the polymer sample containing the antioxidant. The relative amounts of formaldehyde, acetaldehyde, and acetone evolved during oxidation (280°C, 2 min) from samples with and without Irganox B561 were constant (Table II). However, in the presence of the antioxidant the absolute emission of these substances has decreased 9–10 times. A comparison between two antioxidants, a sterically hindered phenol (Irganox 1010), and a combination of a sterically hindered phenol and a peroxide decomposer (Irganox B561) shows that the latter is more effective in depressing the evolution of acetone on oxidation of PP, expecially at 240–280°C (Fig. 7).
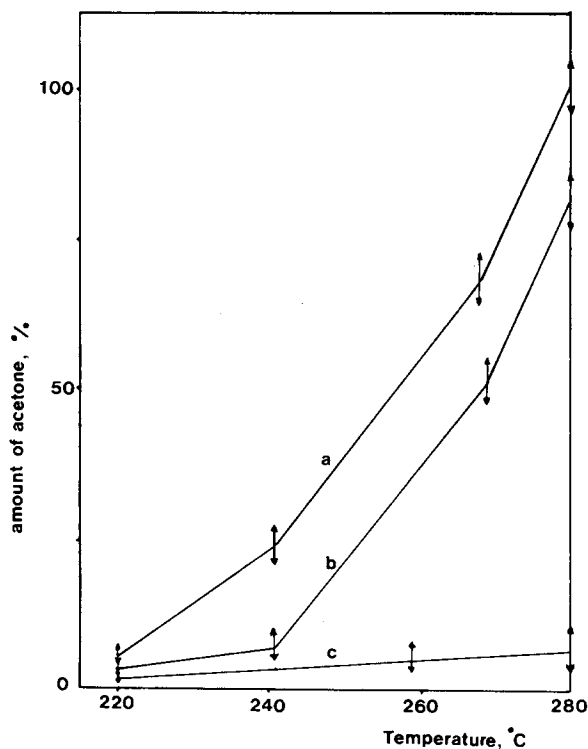
Fig. 7. Temperature effect on the evolution of acetone on the oxidation of PP during 2 min: (a) the original PP film; (b) PP film with Irganox 1010; (c) PP film with Irganox B561.

Oxidation of Polypropylene

Oxidation of PP has been studied thoroughly at temperatures below the melting point of the polymers, i.e., in the temperature range of 120–170°C.[2–15] The phenomenological description of this process based both on the results of kinetic and spectrophotometric studies can be summarized as follows:

Oxygen adsorption is the first step, followed by an almost quantitative formation of hydroperoxides.[15] In the initial stage of PP oxidation (120–130°C, 0.5 h) the main type of functional groups found were only hydroperoxides[21]; with longer periods of oxidation (2 h) also carbonyl groups appear.[21]

The hydroperoxides formed are not isolated groups, as in the case of polyethylene, but sequences of adjacent groups.[8,15] More than 90% of hydroperoxide groups are intramolecularly bonded.[8] These groups are present in sequences of length of two or more.[8,15] The oxidized polymer cannot be regarded simply as a polymeric hydroperoxide.[12] At 120°C, only about 40% of the oxygen absorbed is present in the polymer, the rest being incorporated in the low molecular weight oligomers.[12]

Thermal decomposition of peroxidic groups in the preoxidized PP proceeds by a complex process. The initial fast reaction, which proceeds to 80% overall conversion, was attributed to chain decomposition of adjacent hydroperoxide groups in the polymer, whereas the slow reaction was believed to be due to the

decomposition of isolated hydroperoxide groups.[9] At 125°C, the latter reaction is about 10 times slower than the former.[11] Thus, the decay of adjacent hydroperoxide groups is the main reaction of degenerate chain branching in PP oxidation.[11] Decomposition of hydroperoxides results in chain scission, introduction of functional groups into the polymer chains and formation of volatile products. Only a minor part of the oxygen absorbed by the polymer (ca. 2%) is present in the organic volatiles, the rest being found in the oxidized polymer fragments.[14,18] The amount of volatiles formed is proportional to the concentration of the hydroperoxide groups in the polymer.[2,14] Moreover, the relative rates of formation of volatile products in the oxidation of PP, and in the decomposition of the polymeric hydroperoxides are the same.[2] Thus, it was concluded that the volatiles are formed in the course of decomposition of the polymeric hydroperoxides.[5] On the basis of these data, it does not necessarily follow that the conclusions arrived at for the oxidation of PP at 120–170°C are also valid at considerably higher temperatures (220–280°C), which are typical for the conventional processing conditions of the polymer. Chien and Kiang,[17] who studied the oxidative pyrolysis of PP at 240–289°C have shown that the experimentally found apparent rates of oxidation are in good concordance with the rates calculated on the basis of the kinetic parameters obtained at essentially lower temperatures (70–140°C).[7] The only substantial difference between the low- and high-temperature oxidation was the magnitude of the steady state concentration of hydroperoxide groups at 140°C and 289°C. At the former temperature it was more than one magnitude greater than at the latter temperature. Alternatively, the concentration of peroxy radicals at 289°C was only insignificantly higher than at 140°C. These facts as well as the conclusion made on the basis of oxidation of PP at 120–140°C, that the volatiles evolved are formed in the process of decomposition of polymeric hydroperoxides, support the suggestion that the volatiles found at high temperature oxidation of the polymer are also formed in the course of decomposition of the hydroperoxides. Actually, the comparison of the gas chromatograms for the volatiles formed on oxidation of PP at 120°C, 280°C and the thermal decomposition of the preoxidized PP at 120°C (Fig. 4) shows that the nature of the most volatiles formed is essentially the same, despite the large difference in the temperature of oxidation. The main difference between low and high temperature oxidation is that at low temperature, rather small amounts of short chain volatiles and relatively large amounts of long chain volatiles are formed, while at high temperatures the opposite is true (compare Figs. 1 and 2). However, the relative amounts of the main oxidation products (at 280°C) of PP obtained at vastly different experimental conditions (Table II) are rather close. This comparison is made for oxidation of PP at 280°C, 220°C, 120°C, and for photolysis of PP hydroperoxide[20] at room temperature. The constant values of the relative amounts of the main oxidation products obtained on oxidation of PP in a broad temperature range confirms that the volatiles are formed by decomposition of hydroperoxide groups of PP. The way PP is oxidized (thermally or by means of photooxidation) is in this respect presumably unimportant.

The Role of Hydroperoxides

The study of decomposition of different primary hydroperoxides[22–24] has revealed hydrogen among other decomposition products. Thus, at 100°C n-butyl
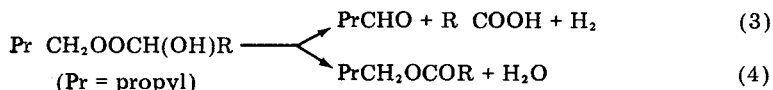
and isobutyl hydroperoxides gave as major products hydrogen (45–50%) and the corresponding acids (n-butyric and isobutyric) together with some esters, water, and small amounts of corresponding aldehydes and alcohols.[24] Wurster et al.[25] found that under these conditions n-butyl deuteroperoxide gave hydrogen, and not deuterium, showing that a carbon–hydrogen rather than an oxygen bond was broken during this reaction:

$$RCH_2OOD \rightarrow RCOOD + H_2 \tag{1}$$
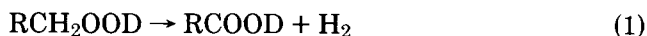
Generation of hydrogen during thermal oxidation of PP and polyethylene at 150°C was also observed by Matveeva et al.[4] It was proposed that a peroxide was an intermediate in the decomposition of primary alkyl hydroperoxides; deliberate addition of an aldehyde to the hydroperoxide caused immediate formation of this intermediate, which normally was produced slowly from aldehyde derived from decomposition of the hydroperoxide itself[26]:

$$BuOOH + RCHO \rightarrow BuOOCH(OH)R \tag{2}$$

It was found that such a peroxide (R=Propyl) at 86°C gave products (hydrogen, butyric acid, butyraldehyde, butanol, and n-butyl butyrate) similar to those obtained from direct decomposition of n-butyl hydroperoxide. The effect of alteration of the group R on the pattern of products was illustrated when R=H (hydrogen, butyraldehyde, formic acid, and butyl formate), and R=CH$_3$ (hydrogen, butyraldehyde, acetic acid, and n-butyl acetate)[26]:

$$Pr\ CH_2OOCH(OH)R \diagup \diagdown
\begin{matrix} PrCHO + R\ COOH + H_2 & (3) \\ \\ PrCH_2OCOR + H_2O & (4) \end{matrix}$$
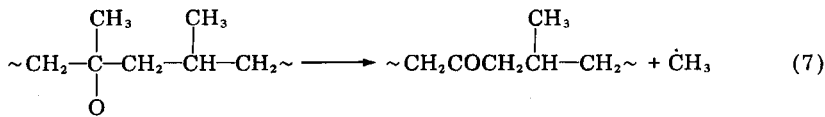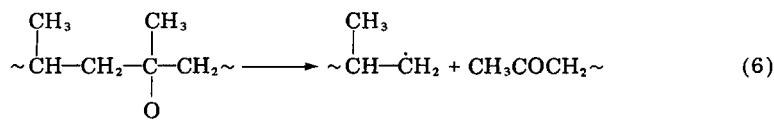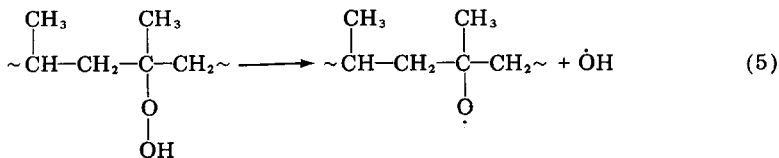
(Pr = propyl)

The evidence for this mechanism of decomposition appears to be very strong, and is in agreement with the earlier interpretation of Rieche,[27] who had observed that the thermal treatment of methyl and ethyl hydroperoxides in the presence of aldehydes yielded hydrogen.

By theory of hydrocarbon oxidation, hydroperoxide would be predicted as the reaction product. The model compound for PP, 2,4-dimethylpentane, oxidizes at 100°C to give hydroperoxide in yields of nearly 90%, based on the oxygen consumed.[28,29] PP oxidation, however, seldom gives hydroperoxide in yields above 40%.[12] The hydroperoxide yield drifts slowly downwards with increasing conversion.[12] Extrapolation to the 0% conversion indicates a primary yield of only 50%.[12] Most of the hydroperoxide groups in PP oxidations are associated with low molecular weight, polar, and soluble molecules. About one half of the hydroperoxides are volatile at 100°C, 0.2 torr.[12] These data allow the presumption that, at considerably higher temperatures, e.g., 220–280°C, the proportion of volatile hydroperoxides could also be expected to be quite large. There is some direct evidence concerning evolution of the volatile hydroperoxides, obtained by measurements of different volatile products formed during conventional processing of polyethylene.[30] The concentration of the peroxides, including hydroperoxides, measured was three times higher than that of the main volatile products: acetaldehyde and formaldehyde together.[30] Thus, it is plausible to presume that these volatile hydroperoxides could to a substantial degree contribute to the formation of the volatiles formed. In this connection, it can be presumed that the volatile hydroperoxides themselves and the products formed by their reactions with aldehydes (formaldehyde and acetaldehyde), e.g.,

reaction (2), would contribute to the formation of formic and acetic acids, reaction (3). As to the acetic acid, the peroxides derived from different ketones may also be responsible. Actually it is known that decomposition of methyl ethyl ketone hydroperoxide,[31,32] catalyzed by acid results in the formation of acetaldehyde and acetic acid, and decomposition of diisopropyl ketone results in the formation of acetone and isobutyric acid.[33]
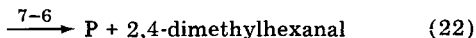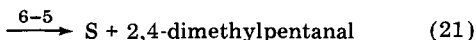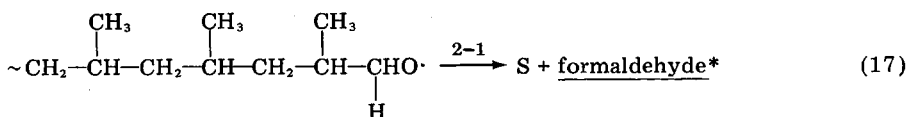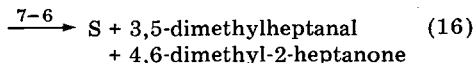
Formation of Volatiles

Hydroperoxides are initial products of oxidation of PP. Decomposition of a hydroperoxide group within the polymer chain eventually results in the formation of an alkyl radical, and a methyl ketone [reactions (5)–(6)]. As was shown by Carlson and Wiles[20] with the photolysis of PP hydroperoxide, the formation of an internal ketone [reaction (7)] is also possible.

$$
\underset{\substack{\displaystyle | \\ OH}}{\underset{\substack{\displaystyle | \\ O}}{\sim CH-CH_2-\underset{\substack{| \\ CH_3}}{C}-CH_2\sim}} \;\underset{\substack{CH_3}}{\overset{CH_3}{}} \longrightarrow \sim \underset{CH_3}{CH}-CH_2-\underset{\substack{| \\ O \\ \cdot}}{\underset{CH_3}{C}}-CH_2\sim + \dot{O}H \tag{5}
$$

$$
\sim \underset{CH_3}{CH}-CH_2-\underset{\substack{| \\ O \\ \cdot}}{\underset{CH_3}{C}}-CH_2\sim \longrightarrow \sim \underset{CH_3}{CH}-\dot{C}H_2 + CH_3COCH_2\sim \tag{6}
$$

$$
\sim CH_2-\underset{\substack{| \\ O \\ \cdot}}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2\sim \longrightarrow \sim CH_2COCH_2\underset{CH_3}{CH}-CH_2\sim + \dot{C}H_3 \tag{7}
$$

The alkyl radicals react with oxygen [reaction (8)], and are eventually converted to alkoxy radicals [reactions (9) and (10)]. The alkoxy radicals can either abstract hydrogen atoms from the PP, thus being converted to alcohols, or they can undergo a fragmentation which is considered to be responsible for formation of different volatile products:
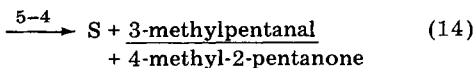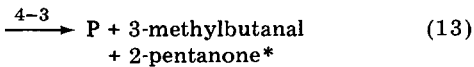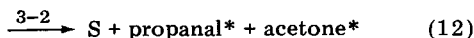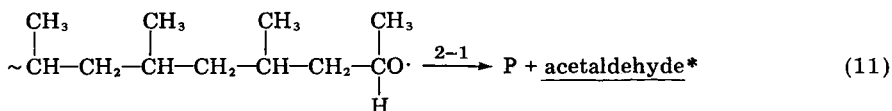
$$
R\text{—}\dot{C}H_2 + O_2 \rightarrow R\text{—}CH_2O\dot{O} \tag{8}
$$

$$
RCH_2O\dot{O} + RH \rightarrow RCH_2OOH + \dot{R} \tag{9}
$$

$$
RCH_2OOH \rightarrow RCH_2\dot{O} + \dot{O}H \tag{10}
$$

The fragmentation of primary and secondary alkoxy radicals, which proceeds via C—C bond scission with or without the transfer of a hydrogen atom or a methyl group, was considered by Chien and Kiang[17] to be responsible for the formation of different volatile products of PP oxidation. The products indicated by an asterisk in the scheme below were found by Chien and Kiang,[17] and the underlined products were identified in the present study. The numbers above the arrow indicates the carbon atoms, the bond between which is broken. The primary and secondary alkyl radicals formed in the course of the fragmentation of alkoxy radicals are indicated as P and S, respectively. Thus, the fragmentation reactions according to Chien and Kiang[17] are:

$$\sim \overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}O\cdot \xrightarrow{2-1} P + \underline{acetaldehyde}* \qquad (11)$$

$$\xrightarrow{3-2} S + \underline{propanal}* + \underline{acetone}* \qquad (12)$$

$$\xrightarrow{4-3} P + 3\text{-methylbutanal} \qquad (13)$$
$$+ \underline{2\text{-pentanone}}*$$

$$\xrightarrow{5-4} S + \underline{3\text{-methylpentanal}} \qquad (14)$$
$$+ \underline{4\text{-methyl-2-pentanone}}$$

$$\xrightarrow{6-5} P + 3,5\text{-dimethylhexanal} \qquad (15)$$
$$+ \underline{4\text{-methyl-2-heptanone}}$$

$$\xrightarrow{7-6} S + 3,5\text{-dimethylheptanal} \qquad (16)$$
$$+ 4,6\text{-dimethyl-2-heptanone}$$

$$\sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{CH}}-CHO\cdot \xrightarrow{2-1} S + \underline{formaldehyde}* \qquad (17)$$

$$\xrightarrow{3-2} P + \underline{propanal}* \qquad (18)$$

$$\xrightarrow{4-3} S + \underline{2\text{-methylpropanal}}* \qquad (19)$$

$$\xrightarrow{5-4} P + 2\text{-methylpentanal} \qquad (20)$$

$$\xrightarrow{6-5} S + 2,4\text{-dimethylpentanal} \qquad (21)$$

$$\xrightarrow{7-6} P + 2,4\text{-dimethylhexanal} \qquad (22)$$

It is plausible to assume that the fragmentation of the highly unstable alkoxy radicals is associated with a rather low activation energy. Consequently, the formation of the volatile products due to these reactions could be expected to be rather insensitive to temperature variations in a quite broad temperature range, as was found in this study. For instance, the activation energy of decomposition of the t-butoxy radical, which results in the formation of a methyl radical and acetone, is reported to be 38 kJ/mol[34]; decomposition of an acetyl radical to a methyl radical and carbon monoxide requires an activation energy of about 63 kJ/mol.[35]

Formation of some other products of PP oxidation can be derived on the basis of decomposition of the hydroperoxide groups within the oxidized polymer chains. Formation of the following products can be explained in this way: 2,4-pentanedione [reaction (23)], methacrolein [reaction (24)], 3-penten-2-on [reaction (25)] and 1-cyclopropylethanone [reactions (26) and (27)]:

$$\sim CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle H}{|}}{O}}{\underset{\displaystyle |}{O}}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle H}{|}}{O}}{\underset{\displaystyle |}{O}}}{C}}-CH_2 \sim \longrightarrow 2 \sim \dot{C}H_2 + 2\ \dot{O}H + CH_3-CO-CH_2-CO-CH_3 \quad (23)$$

$$R-CH_2-\underset{\underset{\underset{\overset{|}{O}}{\overset{|}{O}}}{\overset{|}{H}}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\overset{|}{O}}{CH}-R \longrightarrow 2\ R^{\cdot} + H_2O + CH_2{=}\overset{\overset{CH_3}{|}}{C}-CHO \qquad (24)$$

$$\sim CH_2-\underset{\underset{\underset{H}{\overset{|}{O}}}{\overset{|}{O}}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\overset{CH_3}{|}}{CH}-\underset{\overset{|}{H}}{CH}-CH_2\sim \longrightarrow 2\ \sim\dot{C}H_2 + H_2O + CH_3{-}CO{-}CH{=}CH{-}CH_3 \quad (25)$$

$$CH_3-CO-\underset{\overset{|}{H}}{CH}-\underset{\overset{CH_3}{|}}{CH}-\underset{\underset{\underset{H}{\overset{|}{O}}}{\overset{|}{O}}}{CH}-R \longrightarrow H_2O + RCHO + \left[CH_3{-}CO{-}\dot{C}H{-}\overset{\overset{H_2C-H}{}}{CH}\right] \quad (26)$$

$$\left[CH_3{-}CO{-}\cdot\dot{C}H{-}\overset{\overset{H_2C\cdots H}{}}{CH}\right] \longrightarrow CH_3{-}CO{-}\overset{\overset{CH_2}{\triangle}}{CH}{-}CH_2 \qquad (27)$$
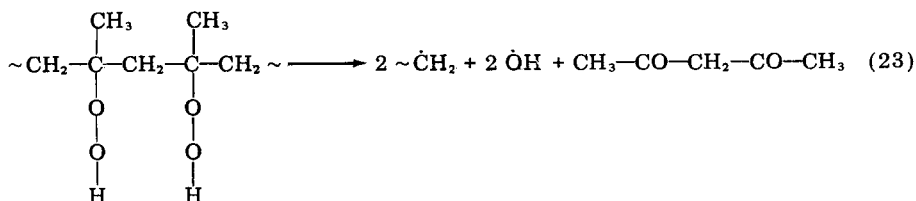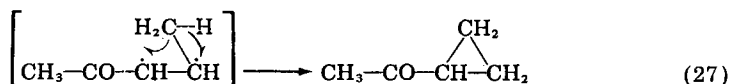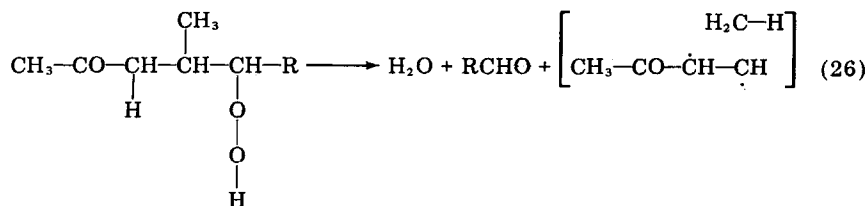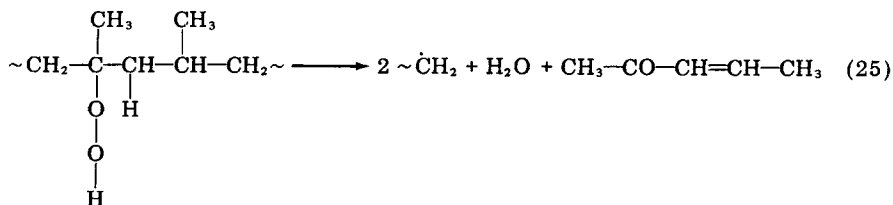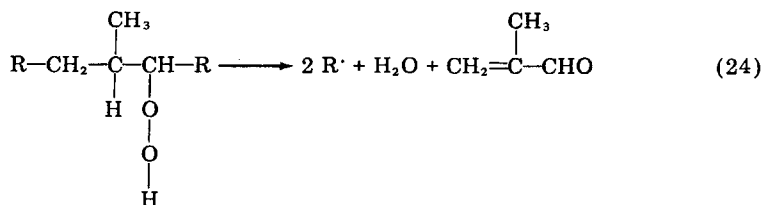
It can be presumed that the formation of 1-cyclopropylethanone proceeds by a mechanism which involves a biradical, reactions (26) and (27). These reactions occur presumably below the surface of the polymer under oxygen-deficient conditions. The mechanism of formation of 3-buten-2-one has been considered by Chien and Kiang,[17] and the formation of 1-hydroxy-2-propanone and 2-methyl-2-propen-1-ol has been discussed elsewhere.[18]

Considering some minor products of PP oxidation such as dimethylbenzene, methyl and dimethylfuran and pentadiene, it should be pointed out that the presence of aromatics,[16] furan derivatives,[14] and dienes[16,17] among the products of PP oxidation has already been mentioned in the literature.

The Role of Antioxidants

The relative amounts of some of the main volatiles formed on the oxidation of polymer samples with and without antioxidant are practically the same (Table II). However, the retarding effect depends on the type of the antioxidants used. The weakest effect is observed with use of a sterically hindered phenol (Irganox 1010); a more pronounced effect is achieved when a combination of a sterically hindered phenol and a peroxide decomposer (Irganox B561) is used (Fig. 7). Even at such a high concentration as 1% (w/w) the presence of the antioxidants does not exclude the oxidative degradation, i.e., the formation of the volatiles at the lowest studied temperature of 220°C. The action of the antioxidants can be expressed in the following way:

$$R\dot{O}O + In{-}H \rightarrow ROOH + In{\cdot} \qquad (28)$$

$$ROOH + P(OR)_3 \rightarrow ROH + O{=}P(OR)_3 \qquad (29)$$
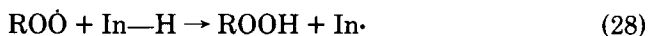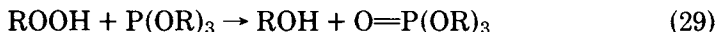
where In—H = antioxidant. The role of a sterically hindered phenol is to convert the peroxy radicals to hydroperoxides. This reaction is competitive with reaction (30) by precluding the abstraction of hydrogen atoms from the polymer chain, and thereby retarding further oxidation, i.e., reaction (8):

$$ROO\cdot + R{-}H \rightarrow ROOH + R\cdot \qquad (30)$$
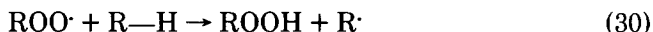
The organophosphite acts as a peroxide decomposer, deactivating the hydroperoxides by a molecular process. At high temperatures (above 200°C) the hydroperoxides are very unstable. In addition, the rate of decomposition of the hydroperoxides is presumably considerably higher than the mobility of the organophosphite molecules which have not succeeded in destroying effectively all the surrounding hydroperoxides.

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