

Thermal Oxidation of Polypropylene Close to Industrial Processing Conditions

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Synopsis

Thermal oxidation of isotactic polypropylene (PP) at 220 and 280°C in air was studied. Gas chromatography–mass spectrometric analysis was used to separate and identify the volatile products of PP oxidation. Twenty-three products were identified and 15 substances were quantified. The aldehydes are the principal products formed, followed by ketones, acids, and alcohols. The main organic product quantified was acetaldehyde. The volatile organic products formed constitute about 3% of the amount of water formed. The relative amounts of the most volatile products formed in the range 220–280°C are practically independent on the temperature of oxidation. The mechanism of formation on the oxidation products is discussed.

INTRODUCTION

Polypropylene (PP) is the fourth main bulk plastic produced in the world after polyethylene, poly(vinyl chloride), and polystyrene. Its growth rate is however the highest among the plastics mentioned. The typical processing temperature of PP is within the range 170–310°C,¹ i.e., at temperatures somewhat higher than that of polyethylene. Generally, PP is fairly stable toward thermal degradation in vacuum at temperatures of about 300°C.² However, the simultaneous effect of high temperature and atmospheric oxygen results in oxidation of the polymer. Compared with polyethylene,² unstabilized PP is especially susceptible to oxidative degradation because of the high reactivity of hydrogen atoms attached to tertiary carbon atoms. The period of time when the effect of high temperature is simultaneous with oxygen access to the polymer surface during processing is fairly short (below 1 min); however, the low thermal conductivity of the polymer can prolong this time. This is especially evident for thick polymer items. Thus, some oxidation, restricted mainly to the polymer surface, takes place. As a result, formation of oxygen-containing volatile products can be expected.

Most of the investigations concerning formation of the volatile products during thermal oxidation of PP were performed at temperatures below the melting point of the polymer, i.e., in the range 120–170°C.^{3–12} The volatile products identified in these studies are mainly oxygen-containing substances, primarily acetone, acetaldehyde, formaldehyde, α -methylacrolein, and 2-ketones. The principal product formed was acetone.^{3–11} Oxidative pyrolysis of PP at higher temperatures was studied by Michal and co-workers (350°C)¹³ and by Chien and Kiang (240–290°C).¹⁴ In the latter work, performed at typical processing temperatures, essentially the same compounds as those in the temperature range 120–170°C were found, although a large number of products separated by GC remained

unidentified. The main substance identified was acetaldehyde. Michal and co-workers¹³ identified 39 products, the amounts of which were presented quantitatively as the peak area relative to the total chromatographic area. The main component was acetone, followed by crotonaldehyde and diacetyl and acetyl acetone. Among the products detected in the course of thermal oxidation of PP, some are quite toxic, e.g., formaldehyde, α -methylacrolein, and crotonaldehyde. Thus, knowledge of the nature and of the amounts of products evolved during thermal oxidation of PP in the upper temperature range of processing is very important for the assessment of the health hazards of the workers involved in PP processing. It is also evident that this information is valuable for elucidation of the mechanism of oxidative degradation of PP.

EXPERIMENTAL

Materials

Shell Polypropylene KM 6100 for general-purpose, molding quality and without additives was used. This is a crystalline, isotactic polymer having the following characteristics: density, 0.905 g/cm³; melt index, 3.5 (2.16 kg at 230°C). Polymer films (50 μ m) were molded at 210–220°C during 60–90 s.

Oxidation Procedure

The analysis of the volatile products evolved during the oxidation of PP was carried out by means of a thermal degradation unit connected to a gas chromatographic–mass spectrometric (GC/MS) system. The thermal degradation unit consists basically of three parts: a thermal degradation tube, a movable furnace, and an enrichment section (Fig. 1) described elsewhere.¹⁵

Polymer films (0.2–0.4 \pm 0.01 mg) were heated to a final temperature of 220 or 280 \pm 2°C during 2 min in dry air at atmospheric pressure. Air flow was maintained at about 34 ml/min. The volatile products formed during the oxidation of PP travel before trapping through a zone where temperature is kept at about 125°C (Fig. 1). Kinetics of the heating of the PP samples are shown in Figure 2.

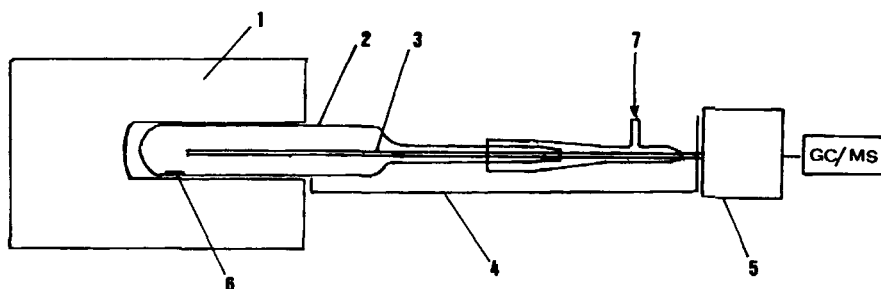


Fig. 1. Thermal degradation sampling system: 1, furnace; 2, thermal degradation tube (200 mm \times 25 mm i.d.); 3, capillary; 4, transfer section (100–125°C); 5, enrichment section; 6, sample; 7, elution gas inlet.

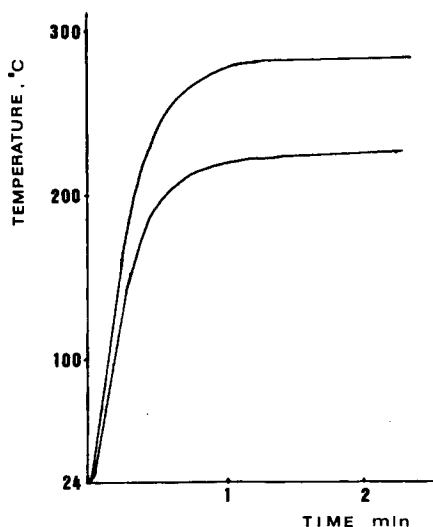


Fig. 2. Kinetics of heating of the samples in the thermal degradation tube.

Apparatus and Procedure of Gas-Chromatographic Separation

The GC/MS system used has been described elsewhere.¹⁵ Separation of the volatile products formed on thermal oxidation of PP was carried out on silanized glass columns (2.0 m \times 1.8 mm i.d.) packed with 6% OS-138 coated on Tenax GC 80/100 mesh and Porapak T 80/100 mesh columns (1.0 m \times 1.8 mm i.d.). A Teflon column (1.0 m \times 1.8 mm i.d.) packed with 8% Fluorad FC-431 and 0.6% H₃PO₄ coated on Tenax GC 60/80 mesh was also used.

Separation on the OS-138 column was performed using the following temperature program: at 30°C for 2 min, then programmed to 120°C at 7°C/min, and from 120 to 190°C at 8°C/min. Separation on the Fluorad FC-431 column was carried out using the following temperature program: at 30°C for 2 min, then programmed to 140°C at 6°C/min.

Separation on Porapak T column was made at isothermal conditions at 110°C. Carrier gas (helium) flow rate was in all cases 20 ml/min.

Quantitation of the volatile products was performed by selected ion monitoring (SIM). Solutions of the individual products (analytical-grade reagents were used) at four concentrations were run, calculations being made graphically by means of calibration plots.

Identification of the substances separated by GC was based on comparison of the mass spectra with those in the literature¹⁶ as well as on comparison of the mass spectra of pure substances and retention times.

RESULTS

The thermal oxidation of PP results in formation of a complex mixture of volatile organic products. The components identified by MS in the course of GC separation are given in Table I; 23 products were identified. Among these, five substances which had not been reported earlier were detected. These products are methyl cyclopropyl ketone, 1-hydroxy-2-propanone, 2-methyl-

TABLE I
 Products Identified by GC/MS Measurements

No.	Substance	<i>m/e</i> Values used for quantitation
1	CO	
2	CO ₂	
3	Water	17, 18
Hydrocarbons		
4	Ethylene	
5	Ethane	
6	Propylene	
7	Isobutylene	
Aldehydes		
8	Formaldehyde	29, 30
9	Acetaldehyde	43
10	Propanal	
11	α -Methylacrolein	41
Ketones		
12	Acetone	43, 58
13	2-Butanone	72
14	2-Pentanone	86
15	1-Hydroxy-2-propanone	74
16	Methyl cyclopropyl ketone	69
17	Acetylacetone	100
Alcohols		
18	Methanol	31
19	2-Methyl-2-propen-1-ol	72
Ethers		
20	2,5-Dimethylfuran	96
Esters		
21	Methyl formiate	Identified by mass spectra according to ref. 16
Acids		
22	Formic acid	46
23	Acetic acid	45

2-propen-1-ol, 2,5-dimethylfuran, and methyl formiate. The oxygen-containing products constitute the absolute majority of the substances identified; hydrocarbons are formed in rather small amounts; among these ethylene, ethane, propylene, and isobutylene were identified.

Fifteen oxygen-containing products were quantified. These include aldehydes, 2-ketones, alcohols, acids, and ether. The results of the quantitative measurements of these products obtained during thermal oxidation of PP at 220 and 280°C are given in Table II. The main product formed during thermal oxidation of PP is water. The amount of water produced is about 33 times that of all organic volatile products found both at 220 and 280°C. When the oxidation temperature is raised from 220 to 280°C, this results in a ca. 20-fold increase in most of the products quantified.

The most abundant organic products found on the oxidation of PP at 220°C are acetaldehyde, acetone, α -methylacrolein, acetic acid, and formaldehyde, and at 280°C acetaldehyde, formaldehyde, acetone, acetic acid, and α -methylacrolein. Acetaldehyde is the main compound produced both at 220 and 280°C.

Relative amounts of the oxidation products of PP formed at different tem-

TABLE II
Amounts of Some Products Formed on Oxidation of PP in Air During 2 Minutes^a

Substance	Amount formed, $\mu\text{mol/g}$ polymer		Ratio of the amounts of products formed at 280 and 220°C
	220°C	280°C	
Aldehydes			
Formaldehyde	16	403	20
Acetaldehyde	25	520	25
α -Methylacrolein	7	126	18
Ketones			
Acetone	12	213	18
1-Hydroxy-2-propanone	1	8	8
2-Butanone	—	8.3	—
2-Pentanone	1.4	33	23
Methyl cyclopropyl ketone	0.8	20	25
Acetylacetone	6	55	9
Alcohols			
Methanol	—	7.5	—
2-Methyl-2-propen-1-ol	—	2.8	—
Ethers			
2,5-Dimethylfuran	0.7	2.7	4
Acids			
Formic acid	—	56.5	—
Acetic acid	9.3	213	23
Organic volatiles total	83	1669	
Water	2700	53000	18

^a The relative standard deviation (R.S.D.) varies between 8.9 and 19% for compounds given in the table, except for acetic acid (R.S.D. 53%) and water (R.S.D. 31%), both at 220°C, i.e., in the lowest concentration range.

peratures are shown in Table III. It can be seen that the substantial increase in the oxidation temperature from 220 to 280°C has very little effect on the relative amounts of the products formed on oxidation of PP.

DISCUSSION

Mechanism of Polypropylene Oxidation

The results of this study should be considered in the relation to the knowledge concerning thermal oxidation of PP so far obtained. The bulk of the investigations of thermo-oxidation of PP has been performed at temperatures below the melting point of the polymer, namely, in the range 120–170°C.³⁻¹² The main conclusions which can be drawn on the basis of these studies are as follows:

- (1) In the initial stage of PP oxidation, the oxygen absorbed leads to an almost quantitative formation of hydroperoxides.¹²
- (2) The hydroperoxide concentration is strongly dependent on the pressure of oxygen rather than on the temperature of oxidation.¹²
- (3) During PP oxidation, formation of hydroperoxide sequences, mainly dihydroperoxides, can be observed.¹²
- (4) An increase in the temperature on PP oxidation results in an increased rate of oxygen absorption. The activation energy of PP oxidation measured on

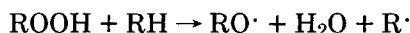
TABLE III
Relative Amounts of Oxidation Products of PP Formed at Different Temperatures

Substance	Relative amount			
	125°C ⁵	135°C ⁵	220°C	280°C
Water	100	100	100	100
Acetaldehyde	1.0	0.8	0.92	0.98
Formaldehyde	1.8	2.0	0.59	0.76
Acetone	3.0	3.1	0.44	0.40
Acetic acid	—	—	0.36	0.40
α -Methylacrolein	—	—	0.26	0.24
2-Pentanone	—	—	0.05	0.06
Methyl cyclopropyl ketone	—	—	0.03	0.04
Acetylacetone	—	—	0.22	0.11
2-Hydroxypropanone	—	—	0.04	0.02
2,5-Dimethylfuran	—	—	0.03	0.005

the basis of oxygen uptake in the temperature range 150–170°C is equal to 21.8 kcal/mol.⁷ At high-temperature oxidation (240–290°C), this value measured on the basis of weight loss of PP is about 16 kcal/mol.¹⁴

(5) There is a linear relationship between oxygen uptake and the volatile products formed.¹¹ Formation of the volatiles is proportional to the peroxide concentration.⁵ The relative rates of formation of volatile products in the oxidation of PP and in the decomposition of PP hydroperoxide are practically the same.⁵ These results show that all the products are obtained as a result of decomposition of PP hydroperoxides.

(6) The experimental results obtained during kinetic studies at 120–140°C give evidence that the polymeric hydroperoxide decomposes in the course of the reaction with the polymer according to the following equation⁶:



The endothermic effect of this reaction (–15 kcal/mol) is 25 kcal/mol less than the endothermic effect of monomolecular decomposition of PP hydroperoxide.¹⁷

(7) The concentration of the volatile products formed depends on the amount of oxygen absorbed rather than on the temperature of oxygen absorption.¹¹

(8) The ratio of the volatile products (water, acetone, acetaldehyde, and formaldehyde) formed in the temperature range 120–140°C is to a small extent dependent on the temperature.⁵

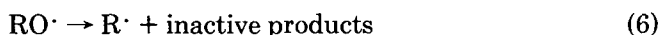
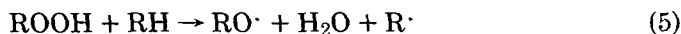
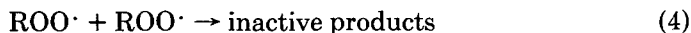
(9) The main volatile organic products observed are acetone, acetaldehyde, formaldehyde, acetic acid, and α -methylacrolein.^{5,11} Other products such as methanol, 2-butanone, 2,4-dimethylfuran, propanal, butanal, and 2-pentanone were also identified.¹¹

While discussing the oxidation of PP at rather high temperatures (220–280°C), some new considerations should be taken in account: (1) the concentration of hydroperoxide groups can be assumed to be low and their stationary value is probably readily reached; (2) the impact of monomolecular decomposition of PP hydroperoxides cannot be neglected. Besides, it should be stated that the formation of organic volatiles in the thermal degradation sampling system probably proceeds, both on the polymer melt and in the gas phase, by oxidation of fragments of decomposed polymer volatile at the experimental conditions. The oxidation in the gas phase takes place under conditions of a certain tem-

perature gradient because the volatiles escaping the polymer melt are cooled in a 200-mm-long transfer section kept at 125°C.

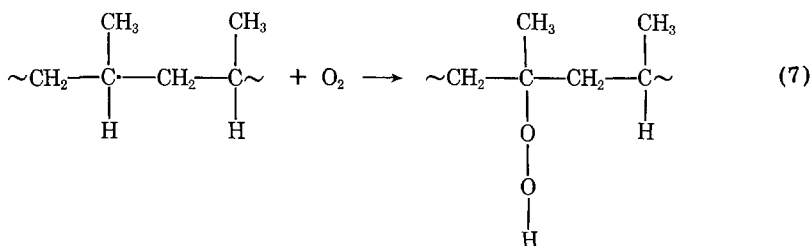
Considering that the volatile products formed during thermal oxidation of PP are generated in the process of decomposition of the polymer hydroperoxide, it is plausible that the conclusions concerning oxidation of PP at 120–170°C are also valid at higher temperatures, i.e., exceeding 200°C. From Table III, it can be seen that the relative amounts of the most volatile products formed in the range 220–280°C are practically independent on the temperature of oxidation, as was found by Pudov and Neiman⁵ at 120–140°C. Moreover, the relative amounts of acetaldehyde formed in the temperature range 120–280°C are constant, although the corresponding values for formaldehyde and acetone differ by about 2.5 and 8 times, respectively. In this connection, it is relevant to mention that Mayo,¹⁸ discussing the results of the effect of temperature on the liquid-phase oxidation of butane, pointed out that “the reactions at low conversions and high temperatures are the same as at low temperatures, but the proportions of the reactions change and in the expected ways.” Further similarities of the oxidation of PP at 120–140 and 220–280°C can be found on comparing the amounts of organic volatiles to the total amount of volatile products formed. The organic volatiles comprise about 3% of the amount of water, which is the main product of PP oxidation.⁷ This value is comparable with the literature data,¹¹ which reveal that the organic fragments constitute about 5–10% of the total volatile products.¹¹ In addition, the oxygen content in the organic volatiles is about 3.5% of that in water. This value shows good agreement with the result that only about 2% of the oxygen absorbed by the polymer is present in the organic volatile products.¹¹

The mechanism of thermal oxidation of PP proposed on the basis of oxidation of the polymer at 120–140°C can be written as follows⁶:

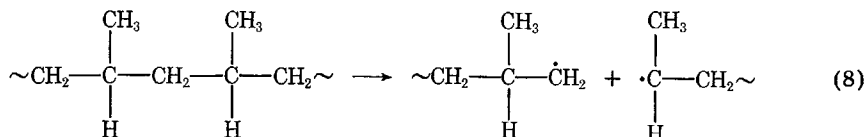


The fragmentation reaction of alkoxy radicals, reaction (6), is considered to be the principal process leading to lowering of the molecular weight of the polymer and to the formation of volatile products.

The weakest C—H bond in PP is the tertiary C—H bond which could be expected to be the initial point of attack. During oxygen uptake at 150–180°C, the following exothermic reaction may occur²:



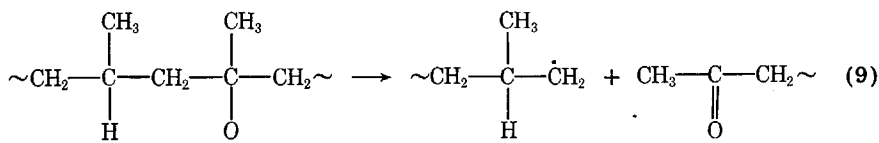
The hydroperoxide formed decomposes according to reaction (5). At temperatures in the vicinity of 300°C, another initiation reaction¹⁴ should also be considered:



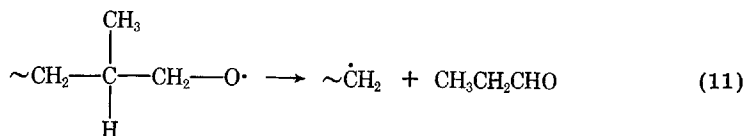
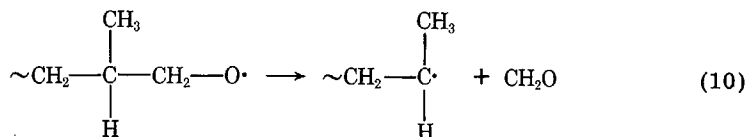
In fact, the experiments made on thermal degradation of PP in helium at 280°C during 2 min have shown formation of hydrocarbons. This confirms that an initiation reaction of type (8) actually takes place. The decrease in activation energy of PP oxidation from almost 22 kcal/mol at 150–170°C⁷ to 16 kcal/mol at 240–290°C¹⁴ is probably due to reactions similar to reaction (8).

The radicals formed in reaction (8) would most probably be converted to alkoxy radicals by the sequence of reactions (2)–(5). The fragmentation of secondary alkoxy radicals leads to the formation of 2-ketones and alkyl radicals,¹⁴ reaction (9):

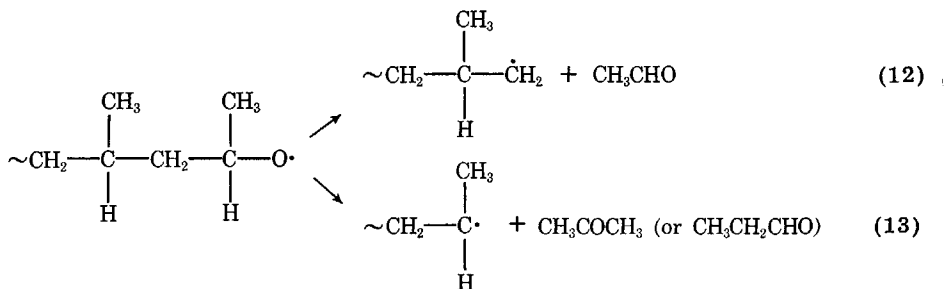
The alkyl radicals, in the presence of oxygen, form peroxides, hydroperoxides, and eventually alkoxy radicals, reactions (2)–(5).



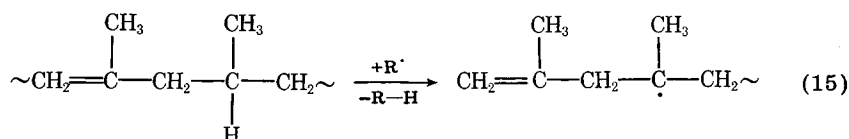
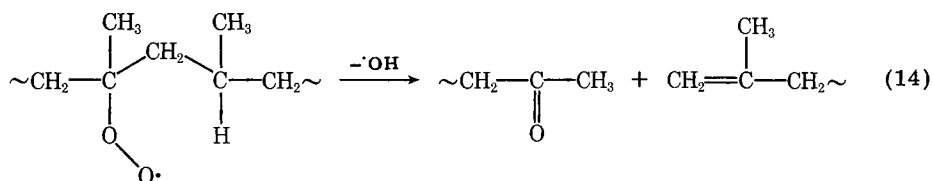
Decomposition of a secondary alkoxy radical can also result in formation of formaldehyde, reaction (10),¹⁷ and propanal, reaction (11)¹⁴:



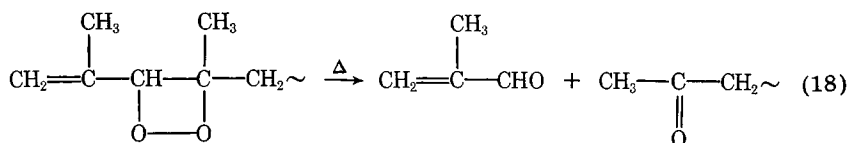
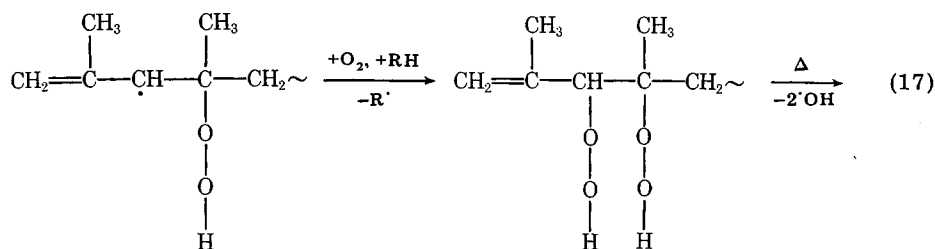
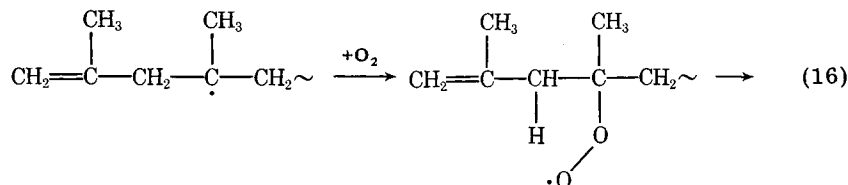
Fragmentation of a tertiary alkoxy radical gives rise to the formation of acetaldehyde, reaction (12), and acetone or propanal, reaction (13). In the reactions (11) and (13), a hydrogen atom or methyl group transfer is implied. Reactions (10)–(13) have been proposed earlier^{14,17}.



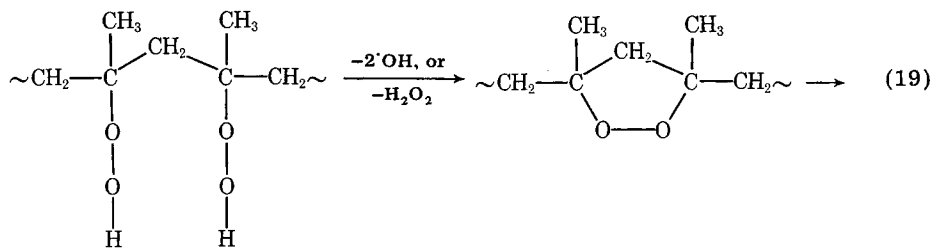
The vinylidene end groups can be formed according to reaction (14), and α -methylacrolein can be generated in the course of reactions (15)–(18). Reactions (14) and (16) imply an intramolecular hydrogen transfer, with a six-membered (14) or five-membered (16) cyclic transition state.¹⁹ The activation energy of these reactions are 17 and 11 kcal/mol for five- and six-membered rings, respectively, for model substances of polyethylene¹⁹:

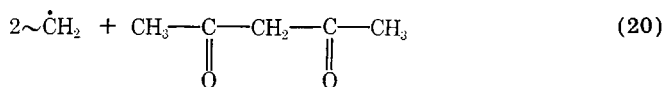


where R· is any radical,

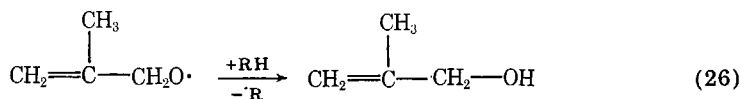
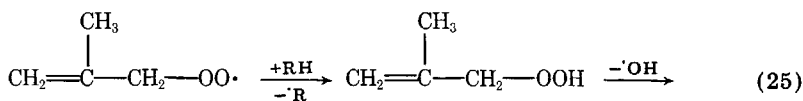
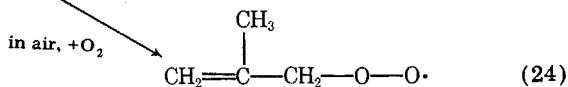
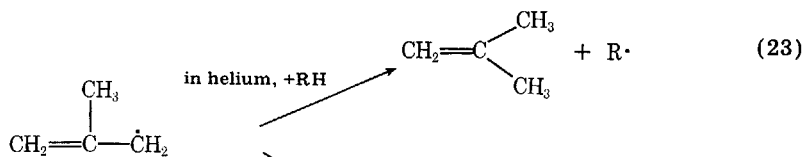
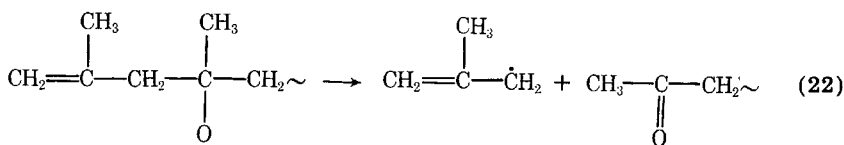
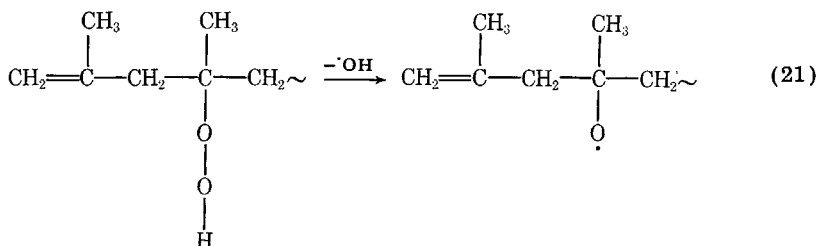


Formation of dihydroperoxide sequences¹² in PP favors probably the generation of acetyl acetone, reactions (19) and (20):

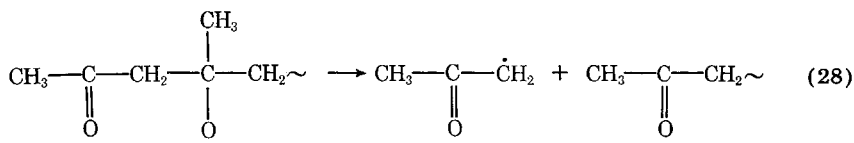
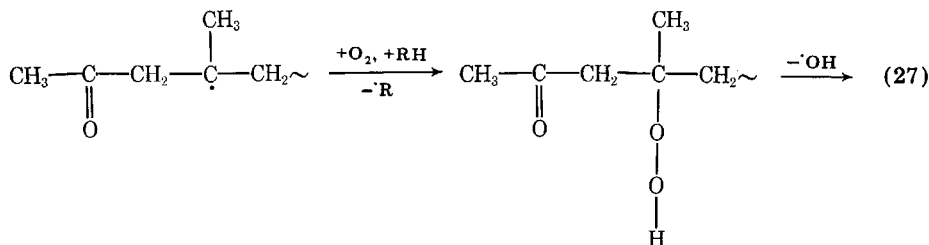


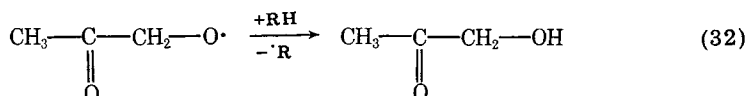
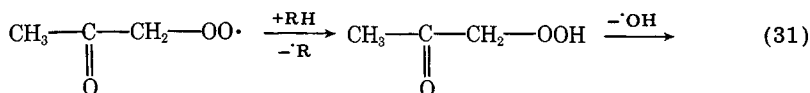
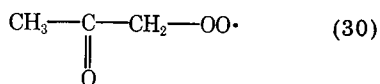
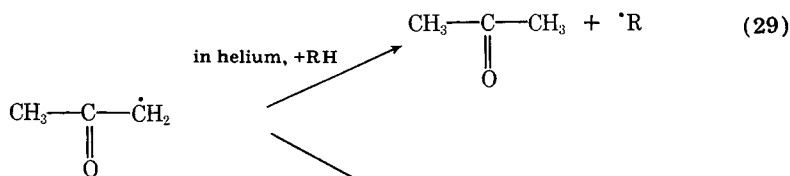


2-Methyl-2-propen-1-ol can be formed in the course of reactions (21)–(26):



Formation of 1-hydroxy-2-propanone can be expected to proceed according to reactions (27)–(32) involving 2-ketones:





Pudov and Neiman⁵ have shown that the yield of the most abundant products of PP oxidation at 130°C formed during decomposition of polymer hydroperoxide depends to a low extent on the oxygen pressure. The rate constants of formation of water, acetone, and acetaldehyde are nearly the same in oxygen (200, 400, and 600 torr) and in helium.⁵ However, it can be assumed that formation of some other minor products of PP oxidation, e.g., 2-methyl-2-propen-1-ol and 1-hydroxy-2-propanone, most likely depends on the presence of oxygen during decomposition of PP hydroperoxide, reactions (23) and (24) and (29) and (30). For instance, decomposition of PP hydroperoxide in an inert atmosphere results in particular in the formation of isobutylene,²⁰ reaction (23), whereas in air 2-methyl-2-propen-1-ol has also been found.

Formation of Acetic Acid

Formation of most abundant products in PP oxidation can be explained on the basis of the decomposition of polymer hydroperoxide. However, there is no plausible explanation for the formation of acetic acid by decomposition of PP hydroperoxide. To verify whether acetic acid is formed directly by decomposition of the polymer hydroperoxide or whether it is formed by oxidation of volatile decomposition products in the gas phase, the following experiments were carried out. PP film (5 mg) was oxidized in air at 150°C during 20 min, after which the reaction tube with the oxidized PP was quickly cooled down to 0°C. The reaction tube was then flushed with helium during 30 min and was at the same time protected from daylight. The volatiles formed during PP oxidation were analyzed by GC. The oxidized PP was heated in an atmosphere of helium at 250°C during 2 min to decompose the hydroperoxides. The volatiles formed were again analyzed by GC. Acetic acid was detected during the oxidation experiment. On the other hand, no acetic acid could be detected during decomposition of polymer hydroperoxide.

Thus, it can be supposed that acetic acid is formed during the further reactions of the oxidized products. Actually, Maizus²¹ who studied the kinetics of the accumulation of peroxides, alcohols, carbonyl compounds, and acids during the

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