

Thermal Oxidative Degradation of Poly(4-methyl-1-pentene). I. Identification of Products and Mechanisms

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Synopsis

Isotactic and atactic poly(4-methyl-1-pentene) powders were degraded in the presence of pure oxygen at temperatures of 145° and 175°C. The functional groups present in the nonvolatile products were identified using infrared spectroscopy. The volatile products that formed were identified by means of a relatively new technique which combines gas chromatography and mass spectroscopy. In this study, seventeen volatile products were detected and identified and their relative abundance estimated. The results obtained could readily be reproduced. Various oxidation mechanisms for these products are postulated.

INTRODUCTION

As part of a series of studies on thermal oxidation of various polyolefins in the bulk phase, the thermal oxidative degradation of isotactic poly(4-methyl-1-pentene) (IPMP) and atactic poly(4-methyl-1-pentene) (APMP) was investigated. Many methods have been utilized to study polyolefin oxidation^{1,2} both in the presence³⁻⁷ and absence⁸⁻¹² of additives. Thus, for example, the rate of formation of nonvolatile products (NVP) has been studied using infrared spectroscopy (IR). Some volatile products (VP) have been identified, mainly for polyethylene and polypropylene, and their hydroperoxide decomposition has been reported (see refs. 1 and 2 for key references).

This paper presents the results of a series of studies on the identification and relative abundance of the volatiles formed during the thermal oxidative degradation of IPMP and APMP using gas chromatography (GC) coupled with mass spectroscopy (MS). The procedure described in this paper was recently used in studying the thermal degradation of polyethylene.¹³ We have modified this procedure in studying the thermal oxidative degradation of isotactic and atactic poly(4-methyl-1-pentene).

EXPERIMENTAL

Materials

An unstabilized pure powder sample of IPMP was used, mp 235°C, density 0.83 g/cc (Imperial Chemical Industries). Upon ignition, an ash content of

0.004% by weight was obtained. A number-average molecular weight of 108,000 was determined by osmometry using a Mechrolab automatic membrane osmometer. APMP was obtained from a double extraction with boiling ether of a commercial poly(4-methyl-1-pentene) (Polysciences). After extraction (1% yield), the APMP was purified several times by standard precipitation procedures and its amorphicity established by x-ray diffraction (powder technique using cylindrical camera). Upon ignition the APMP gave an ash of 0.03% by weight. A number-average molecular weight of 88,000 was determined by osmometry. IR spectrograms were obtained for these APMP and IPMP samples prior to and following oxidation.

Apparatus

The apparatus utilized to identify the VP evolved during the thermal oxidative degradation of IPMP and APMP consists of two instruments connected in series: a thermal chromatograph (MP-3) (Chromalytics, Division of Spex Industries) and a mass spectrometer (GC/MS) (Bendix Scientific Instruments). In Figure 1 is shown the sample chamber which consists of a $\frac{3}{16}$ -in. quartz tube surrounded by a movable furnace. Figure 2 depicts a block flow diagram from the MP-3 apparatus. In the normal usage of the instrument (thermal degradation studies), all the three gas supplies are helium. However, in this investigation, for the first time, the gas supply 1 was switched to pure dry oxygen at a rate of 30 cc/min. The GC unit consisted of a stainless steel column packed with a substrate of 10% Carbowax 20M on 80/100 mesh Chrom WAW which was heat conditioned at 240°C prior to use. All the chromatograms were obtained employing a programmed temperature mode from 20° to 200°C at a rate of 8°C/min and a recorder speed of $\frac{1}{8}$ in./min. In essence, the apparatus employed introduces an expedient concept in oxidative and thermal degradation analysis, since it derives its practicality by coupling two different but compatible techniques.

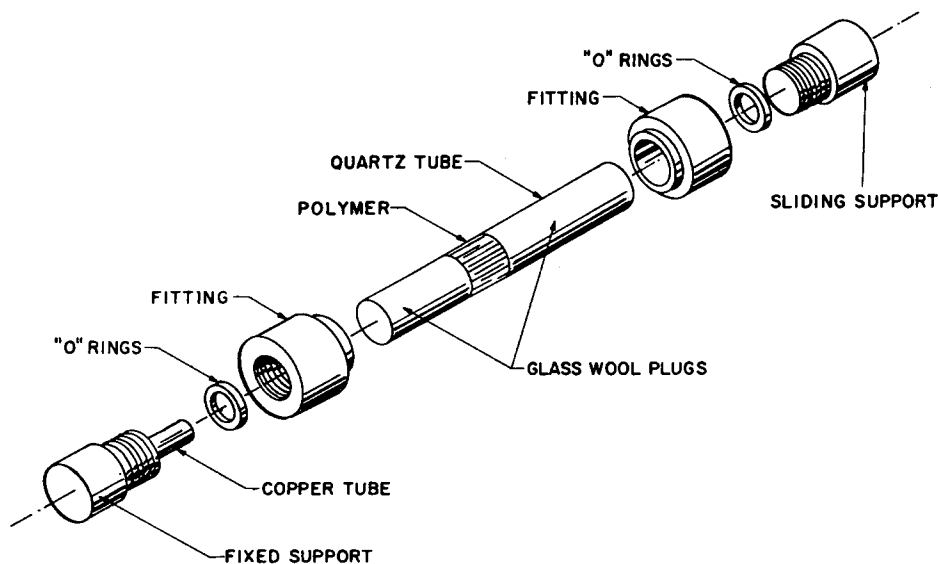


Fig. 1. Sample chamber.

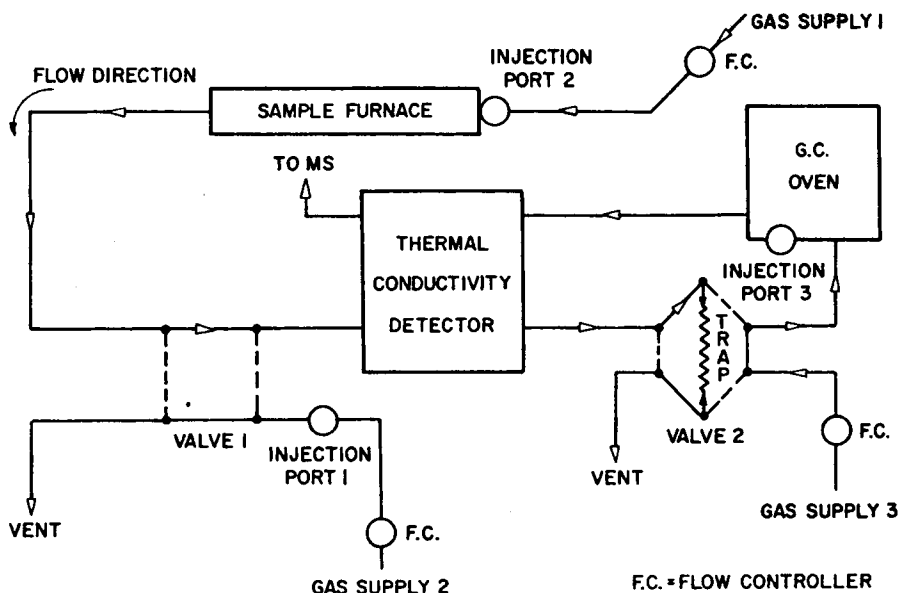


Fig. 2. Block flow diagram of MP-3 apparatus.

Procedure

The polymer sample was inserted into the quartz tube between two glass wool plugs (previously heat treated) in order to position the sample and prevent mechanical loss due to gas flow. After assembly (using Teflon O-rings and swagelok fittings), the sample was initially purged with helium, and the furnace (preheated to the desired temperature, 145° or 175°C) was moved into a position over the sample.

About 100 mg IPMP and APMP were oxidized in the presence of pure dry oxygen (30 cc/min) over reaction periods of 2, 5, 10, 15, and 20 min. The resulting VP were rapidly swept from the sample tube through the thermal conductivity (TC) detector, and to the trap (packed with Porapak Q) across valve 2. In order not to damage the TC due to the corrosive atmosphere of the oxygen, it was kept inoperative during the oxidation. At the end of the oxidation, the VP that had collected in the trap were back-flushed with helium into the GC (now TC in operation). Seventeen VP fractions were detected and identified by retention times, MS, and peak enhancement (injection of known materials through port #1 in order to observe an increase in the GC peak). Several repeat runs indicated excellent reproducibility of results. Further, by using IR prior to and following oxidation, NVP formation could be assessed in terms of hydroxyl-, carbonyl-, and vinyl groups (cf. Fig. 3). Though methane was detected in MS, this study concerned itself only with the identification of the polar volatile products.

RESULTS

A representative gas chromatogram of the IPMP oxidized at 145°C for 10 min is shown in Figure 4. The relative abundance, h_p/h_{CO_2} , of the volatiles

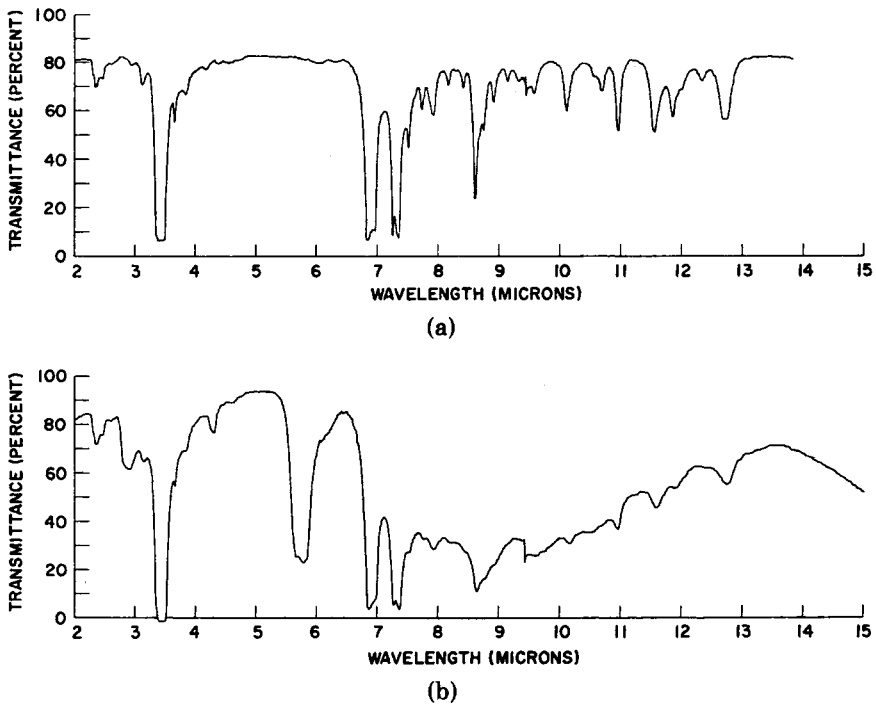


Fig. 3. (a) IR spectrum of IPMP unoxidized. (b) IR spectrum of IPMP oxidized at 145°C.

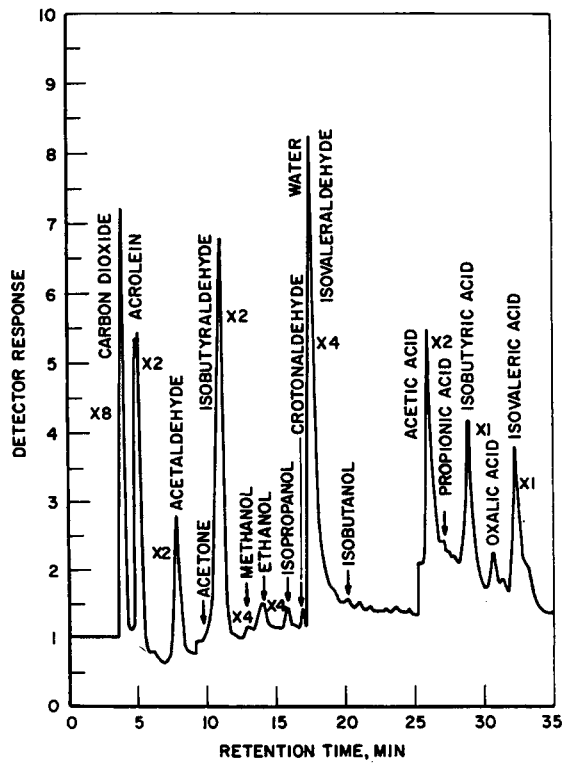


Fig. 4. A representative gas chromatogram of VP of IPMP oxidized at 145°C.

TABLE I
Relative Abundance of VP of Poly(4-methyl-1-pentene)^a

Volatile products	APMP (145°C) ^b	IPMP (145°C)	IPMP (175°C) ^b
Carbon dioxide	1 (47)	1 (42)	1 (41)
Water + isovaleraldehyde ^c	0.42 (2)	0.37 (16)	0.42 (17)
Isovaleric acid	0.03 (1)	0.04 (2)	0.05 (2)
Isobutyraldehyde	0.35 (17)	0.033 (14)	0.25 (10)
Isobutyric acid	0.03 (1)	0.04 (2)	0.06 (3)
Acetic acid	0.10 (5)	0.13 (5)	0.17 (7)
Acetaldehyde	0.03 (1)	0.08 (4)	0.04 (2)
Acetone	0.03 (1)	0.02 (1)	0.15 (6)
Acrolein	0.05 (2)	0.18 (7)	0.17 (7)
Ethanol	0.03 (1)	0.04 (2)	0.03 (1)
Isopropanol	0.03 (1)	0.04 (2)	0.01 (0.5)
Crotonaldehyde	0.03 (1)	0.04 (2)	0.05 (2)
Methanol	—	0.03 (1)	0.01 (0.5)
Isobutanol	—	0.02 (1)	—
Propionic acid	—	0.004 (0)	0.04 (2)
Oxalic acid	—	0.02 (1)	—
Σ	2.13	2.38	2.45

^a The numbers in parenthesis indicate the relative percentage abundance while the remaining values denote peak height relative to carbon dioxide peak height (h_p/h_{CO_2}).

^b Based on TGA measurements (isothermal mode) over 2 hr. APMP and IPMP lost 3% wt. at 145°C and IPMP lost 13% wt. at 175°C in the presence of pure dry oxygen.

^c Water and isovaleraldehyde overlap.

was calculated from the peak heights h of an oxidation product p to that of CO_2 (the first product appearing in the chromatogram and the most abundant). Values of h_p/h_{CO_2} are presented in Table I. In this table, the VP are listed in the order of their relative percentage abundance; and where the VP are chemically similar, e.g., aldehyde and its corresponding acid, these materials follow one another. The carbon dioxide peak was arbitrarily assigned a value of unity (in all runs depicted in Table I, the actual CO_2 peak heights possessed nearly the same values per unit weight of polymer sample used). The major VP (>2%) of the thermal oxidative degradation of poly(4-methyl-1-pentene) are: carbon dioxide, water (+-isovaleraldehyde), isobutyraldehyde, acetic acid, acetaldehyde, acetone, and acrolein. At 145°C, the relative abundance of most of the VP is greater for IPMP compared to APMP. This indicates that IPMP is more susceptible to oxidation than APMP under similar experimental conditions. This observation lends further support to the suggestion made that in aggregated IPMP crystals,¹⁴ oxidation preferentially selects chain folds as reaction sites since the strained backbone configuration would reduce the energy of activation for reaction. The suggestion was based on low-angle x-ray scattering of oxidized films of IPMP. It is noteworthy to mention that in the case of poly(1-butene) the isotactic form had a lower energy of activation than the atactic polymer for oxidation.¹²

Besides VP, it was ascertained that NVP formed during oxidation, by means of IR. Thus, from Figure 3b, it can be seen that a strong band appeared at 2.85μ due to the presence of hydroxyl groups. A triplet formation in the carbonyl stretching region (5.70 – 5.85μ) indicated the presence of such functional groups as aldehyde, ketone, and carboxylic acid,¹⁵ and a band in-

growth at 11.35μ indicated the formation of substituted vinylidene double bonds.¹⁶ (These bands were further supported by the presence of a 6.10μ band.)

DISCUSSION

It has been reported¹⁶ that, during the oxidation of IPMP utilizing air and TGA-MS analysis at temperatures between 140° and 230°C , little, if any, VP are formed at 140°C based on MS data. As the oxidation temperature was increased, MS data indicated that water formed at 200°C and above along with acetyl and acetone ions plus some low molecular weight hydrocarbon fragments (these hydrocarbons were not identified). A major disadvantage of the TGA-MS analysis reported for IPMP oxidation¹⁶ lies on the fact that higher molecular weight VP can be fragmented by MS to lower molecular weight molecules, thereby not revealing primary VP of oxidation. Thus, poly(4-methyl-1-pentene) oxidation can lead to VP, such as isobutyraldehyde, isobutanol, and acetone (as indicated in this work, cf. Table I). Upon subjecting these VP to MS analysis, each of these materials would yield a major fragment which would each possess a molecular weight¹⁷ of 43 (which was attributed¹⁶ to acetyl ion resulting only from acetone fragmentation). The ratio of peak intensities of the major fragment (mol. wt. 43) to the respective parent compound is, for isobutyraldehyde, 2.8; for isobutanol, 2.0; and for acetone, 3.0.

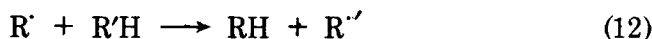
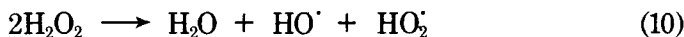
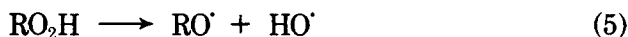
From Table I, the major VP of IPMP and APMP oxidation is carbon dioxide. Although it was not detected,¹⁶ ample evidence for its formation during oxidation of polyolefins was previously reported.^{18,19} During the oxidation of isotactic polypropylene,¹⁹ besides carbon dioxide, water, formaldehyde, acetaldehyde, acetone, and methanol were formed.

Recently, the thermal degradation^{20,21} of poly(4-methyl-1-pentene) was investigated in vacuo over a temperature range of 291 – 341°C . The percentage composition, vol-%, of the fraction volatile at room temperature was found to be (using the reaction temperature of 315°C as an example): isobutene, 57.4; propane, 34.0; isobutane, 3.8; 4-methyl-1-pentene, 1.9; isopentane, 1.4; and ca. 1.5 vol-% of other VP. The major VP consist of isobutene, propane, and isobutane (~95%). The mechanisms involved in the degradation of IPMP, in the absence of oxygen, may be of aid in postulating mechanisms for the oxidative degradation of poly(4-methyl-1-pentene). Accordingly, it would be plausible to assume that the free radicals involved in the formation of isobutene and isobutane during thermal degradation would yield oxygenated VP in the presence of oxygen. From free radicals leading to isobutene and isobutane could be formed derivatives such as isobutyraldehyde, isobutanol, and isobutyric acid (these VP were observed, cf. Table I). Similarly, from free radicals leading to propane could be formed VP in the presence of oxygen, such as acetone.

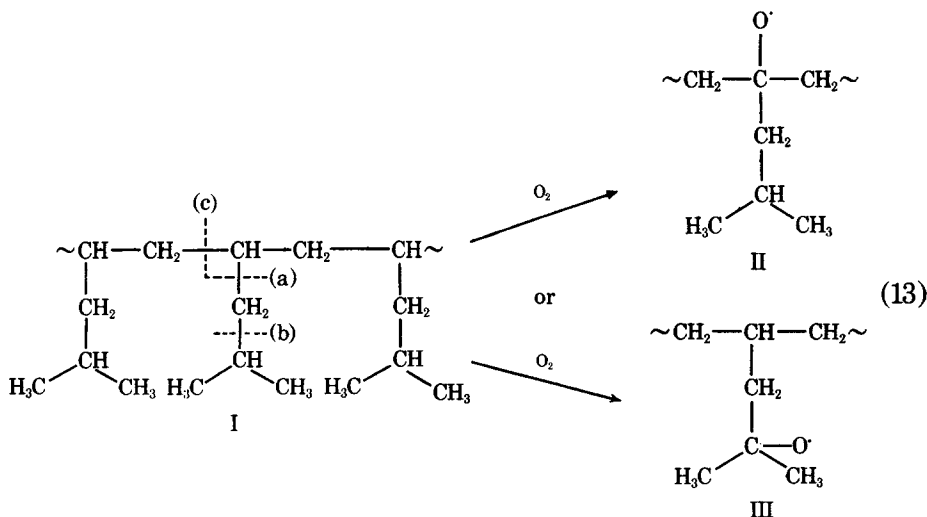
MECHANISMS

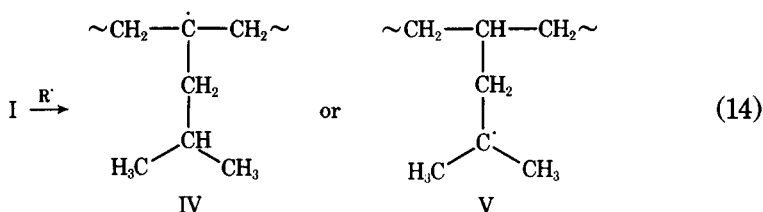
Prior to discussing the various oxidation mechanisms which could lead to the various VP and NVP formed during the thermal oxidative degradation of

poly(4-methyl-1-pentene), the following general and pertinent equations are given^{1,2,22-25}:

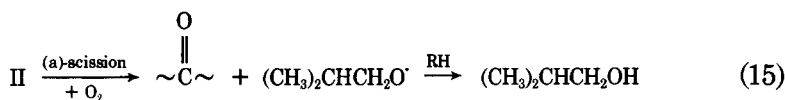


As previously mentioned, the major VP identified were: carbon dioxide, water, isobutyraldehyde, acetaldehyde, acetic acid, acetone, and acrolein. The formation of these products will be discussed first, not necessarily in the order listed. The poly(4-methyl-1-pentene) molecule possesses tertiary hydrogens on the main chain and on the side chain. These hydrogens should be more readily abstracted by free radicals and oxygen than the neighboring secondary hydrogens. Nevertheless, it should be noted that secondary hydrogens would also be expected to participate in reactions which involve tertiary hydrogens albeit to a lesser extent:

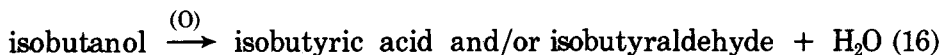




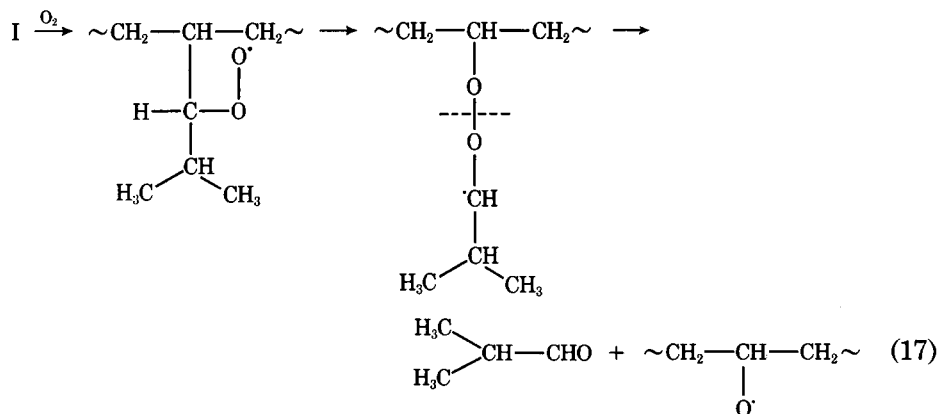
In the preceding, the IPMP moiety I is considered to form two isomers of alkoxide radicals from the tertiary hydrogen on the main chain II and the tertiary hydrogen on the side chain III. These alkoxides can form according to eqs. (1)–(3) and (5). Further, I may react with one of many free radicals present, according to eq. (12), to yield main-chain and side-chain radicals, IV and V, respectively. The dotted lines on structure I indicate bonds which may undergo scission, and also apply to structures II–V:



The resulting nonvolatile ketone could represent ketones detected by IR in the IPMP residue following oxidation. The resulting isobutanol has been identified (cf. Table I) and may undergo further reaction,



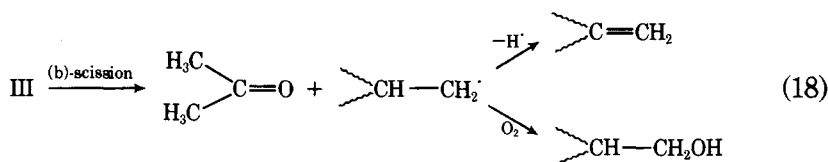
Isobutyraldehyde, a major product, may also be derived in the following manner, which involves secondary side-chain hydrogen and an isomerization,²² cf. eq. (4):



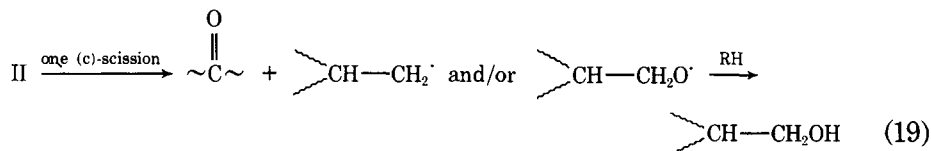
The resulting isobutyraldehyde in eq. (17) can undergo oxidation to the corresponding acid while the resulting alkoxide may either liberate H[•] to form a ketone or may abstract a hydrogen to form the corresponding alcohol (hydroxyl groups have been detected by IR).

The formation of water probably occurs by several routes. Some of these are depicted in eqs. (8), (10), and (16).

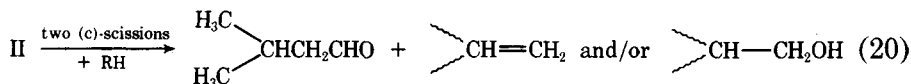
Acetone may form in the following manner:



As previously indicated, vinylidene groups have been detected by IR (11.35 μ band). These groups may be also obtained as follows:

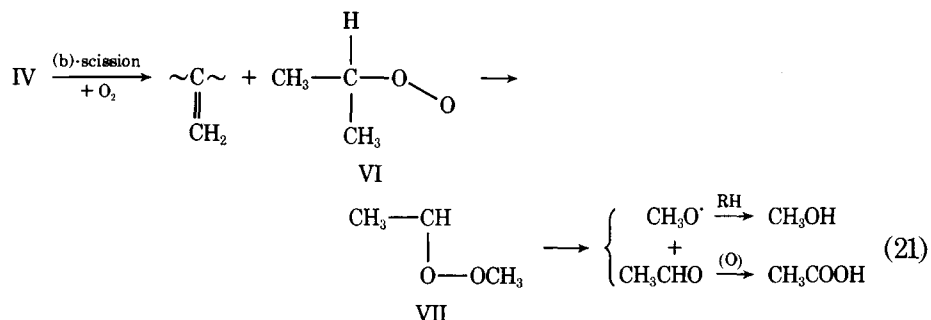


In eq. (19), only one (c)-scission was postulated. If two such scissions are assumed, one of the VP identified, isovaleraldehyde, may form:



The resulting isovaleraldehyde may undergo oxidation to yield the corresponding acid (one of the VP identified).

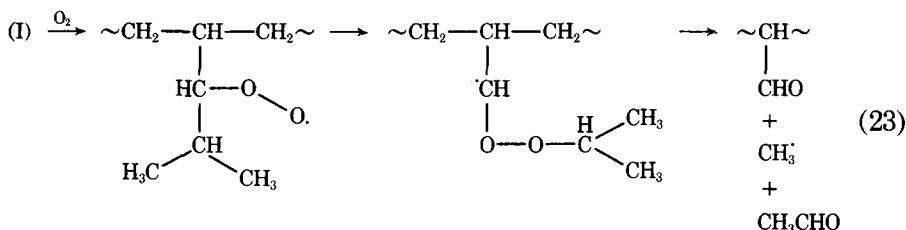
A major product, acetaldehyde, may be obtained from an isomerization reaction (22) similar to that previously described, cf. eq. (17):



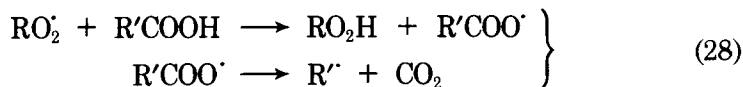
In eq. (21), the formation of acetic acid and methanol along with acetaldehyde is depicted. The resulting acetaldehyde may undergo an aldol condensation to yield the observed crotonaldehyde:



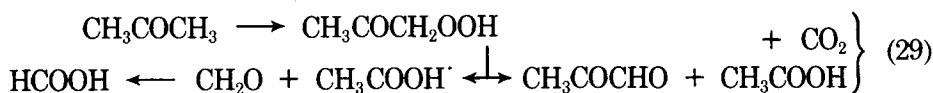
Besides forming in eq. (21), acetaldehyde may also form from involvement of secondary hydrogens, cf. eq. (17):



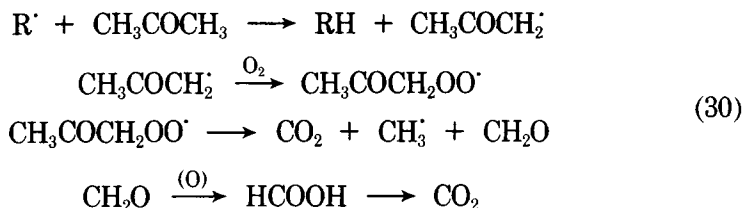
Decarboxylation of acids themselves may occur in the presence of peroxy radicals (24).



In these reactions, the functional groups affected may reside in VP and/or NVP. Due to various reactions it can undergo, acetone²⁴ can lead to carbon dioxide formation as depicted below:



Other reactions involving acetone are²⁷



where R \cdot may represent CH₃ \cdot ; for example.

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