

Thermo-Oxidative Degradation of Low-Density Polyethylene Close to Industrial Processing Conditions

A. HOFF and S. JACOBSSON, *Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden, and Department of Analytical Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden*

Synopsis

Thermo-oxidative degradation of low density polyethylene (LDPE) at a low degree of volatilization (about 4%) at 264–289°C was studied. Gas chromatography–mass spectrometric analysis was used to separate and identify the products of LDPE decomposition. Altogether 44 compounds representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters, and hydroxycarboxylic acids were identified. Sixteen oxygen-containing products were quantified. Among the components identified, the fatty acids and aldehydes predominated. The most abundant product was formic acid. The mechanism of formation of the degradation products is discussed.

INTRODUCTION

Considerable research has been devoted to the thermo-oxidation of polyethylene (PE). Prediction of useful service life of PE compositions and knowledge of the mechanism of elementary steps of oxidation of PE at relatively low temperatures are very important topics in these studies. In addition, the generation of gaseous combustion products in fires, especially poisonous gases, has been recognized as a serious problem. The majority of investigations concerning the volatiles formed during thermo-oxidative degradation of PE have been performed at temperatures of 150–200°C^{1–4} or under pyrolysis conditions at temperatures above 350°C,^{5–7} i.e., exceeding the industrial conditions. The temperature range of 284–355°C have also been studied.^{8,9} However, no information concerning volatiles formed during degradation of PE has been published. Most of those processing methods for PE are performed at temperatures between 200°C and 320°C. The increasing demands of safe production conditions with respect to the health of workers employed in the plastic industry necessitate knowing the nature of volatiles which could be evolved during conventional processing. This includes the temperature range mentioned above, short time spans, and a low degree of volatilization. The most dangerous toxic gases formed during thermo-oxidation of PE are oxygen-containing low molecular weight products such as aldehydes, ketones, and acids. There is information in the literature stating that certain toxic compounds such as formaldehyde, formic acid, acrolein, and acrylic acid among others are formed during the thermo-oxidation of PE.^{1,2,5,6} Therefore, the objective of this study is to identify and quantify the dangerous toxic products evolved during normal processing conditions.

It should be mentioned that the knowledge of the composition and the relative

amounts of the volatiles evolved at thermo-oxidation of PE could also yield more information about the mechanism of the elementary steps.

To identify and quantify the volatiles formed during thermo-oxidation of PE gas chromatography-mass spectrometric analysis (GC/MS) was used.

EXPERIMENTAL

Materials

The low density polyethylene (LDPE) used, Unifos DFDS 6600, was supplied by Unifos Kemi AB, Stenungsund, Sweden. It was a high-pressure product produced in a tubular reactor and free from additives. It has following characteristics: density, 0.922 g/cm³; melt index, 0.31 g/10 min; $\bar{M}_W = 97 \times 10^3$ (GPC)⁸; and $\bar{M}_N = 31 \times 10^3$ (GPC).⁸

Apparatus

A LKB 9000 GC/MS apparatus with a laboratory-made gas chromatograph equipped with an Altema MID (multiple-ion detector) was used. The operating conditions were as follows: ion source temperature 230°C; accelerating voltage 3500 V; trap current 40 μ A. The transfer line and the two-state jet-separator were kept at 220°C. The selected ion monitoring (SIM) chromatograms were recorded on a three-channel strip chart recorder (Linear 595 instrument). The total ion current (TIC) chromatograms were recorded at ionization energy of 20 eV, and SIM chromatograms were recorded at ionization energy of 70 eV. Mass spectra were obtained with an ionization energy of 70 eV. Normalized mass spectra were received by an interfaced laboratory-programmed M-8 Intertech-nique computer and displayed on a TV screen. Scan limits in the range 20–250 m/e were used.

Oxidation Procedure

The generation of the volatile products were carried out with a thermal degradation system, which consists of three parts: a thermal degradation tube, a movable furnace, and an enrichment section (Fig. 1). The polymer sample¹¹ is located in the tube of Pyrex glass (4), which is loosely connected to a T-piece junction (3). The flow rate of helium is set to 40 mL/min. Simultaneously the pump (9), which is regulated to give a flow rate of 20 mL/min is started. The additional flow by-passes the opening of the glass tube and thus precludes diffusion of laboratory air into the glass tube. The thermal degradation is started when the furnace (5) is moved into the position shown in Figure 1(a). The volatiles evolved are enriched on the glass beads in the glass trap (8), which is cooled by liquid nitrogen. The trap (about 230 μ L) and the glass beads (40/60 mesh) are silanized. The trap is attached to a six-port valve (7). The injection of the volatiles into the gas chromatograph is performed as follows. The furnace is withdrawn, the liquid nitrogen taken away, and the valve switched to the position shown in Figure 1(b). At the same time the glass trap is heated to 200°C within 3 s, and the enriched compounds are injected into the column. The constructed apparatus, which consists of highly inert materials (glass, Teflon, tantal) is simple

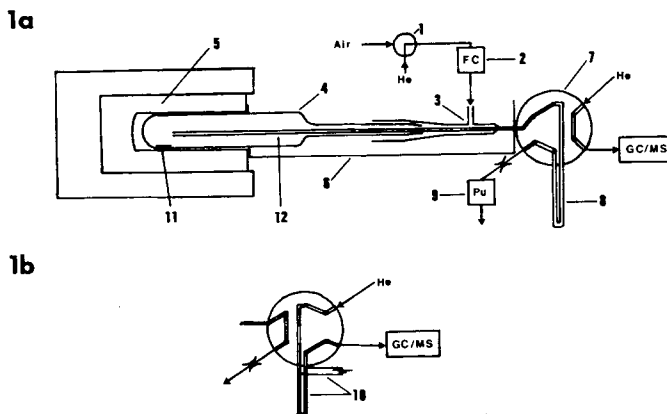


Fig. 1. Thermal degradation sampling system 1 = three-port valve; 2 = flow controller (0–100 mL/min), Porter DFC 1400; 3 = T-piece junction made of glass; 4 = thermal degradation tube made of Pyrex glass; 5 = thermostated, movable aluminum block furnace (0–600°C); 6 = transfer section kept at 125°C; 7 = six-port valve (Carle 2821) kept at 150°C; 8 = glass trap; 9 = pump; 10 = thermostated electric heating spiral; 11 = sample; 12 = capillary

and versatile, and enables one to obtain reproducible results. The flow through the degradation tube can be varied between 0 and 100 mL/min. This can be effected in two ways: (a) by sealing the tube with a teflon tube and a spring to the T-piece junction and regulated by the flow controller; (b) by connecting the degradation tube loosely to the T-piece junction and varying the flow rate through the pump with the variable restriction between valve and pump. When using the pumping arrangement, air could be used as atmosphere even if the glass trap is cooled with liquid nitrogen so that no freeze-out of oxygen occurs. This is due to the slightly reduced pressure in the glass trap. The reduced pressure is achieved by inserting a restriction (glass wool) in the glass capillary between the degradation tube and the valve. The temperature of the transfer section could be easily changed and thus serve as a trap of high boiling compounds, which otherwise could cause severe background problems in the course of GC/MS experiments.

Polymer samples (2.8 ± 0.2 mg) were heated to a final temperature of 264°C, 274°C, 280°C, and 289°C during 4 min in dry air atmosphere; air flow was kept 20 mL/min; kinetics of the heating of the samples in the pyrolyzer are shown in Figure 2. The samples were stamped out to have approximately the same surface area. Before and after the degradation experiments the samples were weighted on a Cahn thermobalance GR-HV. The observed weight loss of the samples during degradation is ca. 4% at 280°C.

Gas Chromatographic Separation

Separation of the thermo-oxidation degradation products of PE was performed 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 or Carbopack C 80/100 mesh coated with 0.2% SP-1000. Used also were a Teflon column (1.0 m \times 1.8 mm i.e.) packed with 8% Fluorad FC-431,¹¹ a fluorocarbon surfactant, and 0.6% H₃PO₄ coated on Tenax GC 60/80 mesh and a Porapak T 80/100 mesh column (1.0 m \times 1.8 mm i.d.).

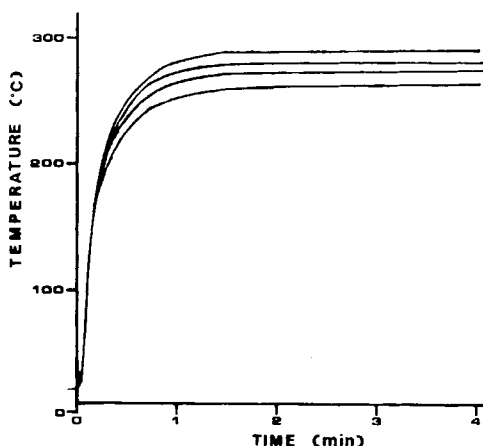


Fig. 2. Kinetics of the heating of the samples in the thermal degradation tube.

Separation on the Carbowack C and OS-138 columns were performed using the following temperature program: at 30°C for 4 min, then programmed to 150°C at 7°C/min, and from 150°C to 210°C at 8°C/min. Carrier gas flow rate was 20 mL/min.

Separation on the Fluorade FC-431 column was performed using the following temperature program: at 30°C for 2 min, then programmed to 140°C at 6°C/min. The flow rate of helium was 20 mL/min.

Separation on Porapak T column was performed at isothermal conditions at 130°C, and at the same flow rate of helium as indicated above.

Quantitative Measurements of the Volatile Organic Products Formed during Thermo-oxidation of PE

a. Aldehydes (Propanal, Butanal, Acrolein, and Pentanal)

The chromatographic separation was performed on the OS-138 column. For butanal and pentanal the following ions were monitored: m/e 29, m/e 30, and m/e 31. For acrolein, propanal and acetone ions with m/e 56, m/e 57, and m/e 58 were used. Standard solutions of the individual products at four concentrations were run. The calculations of the compounds evolved during thermo-oxidation of LDPE were made graphically by means of the calibration curves. The quantitative determination of acrolein, propanal, and acetone on the column used seemed to be quite difficult because all three components appeared almost as one peak on the chromatogram. In recording the chromatogram on the three-channel recorder at the above-mentioned values of m/e for these samples, three peaks with retention times 670 s (m/e 56), 677 s (m/e 57) and 678 s (m/e 58) were obtained. The first peak belongs undoubtedly to acrolein, because the theoretical ratio of the abundances of ions m/e 56/ m/e 57 is about 5.2 for acrolein,¹⁰ as it was found, while it is only 0.06 for propanal and 0.1 for acetone. The amount of acetone was calculated as described below in the point c. To determine the amount of propanal the ion m/e 58 was used. By taking into consideration the quantity of acrolein and acetone found and by building the calibration curves for all three substances, it was possible to find the peak area of ion m/e 58, which is due to propanal, and thereby calculate the amount of propanal.

b. Acids and Acetaldehyde

The chromatographic separation was performed on the Fluorad FC-431 column. The ions m/e 45 and m/e 46 were used for detection of acids, and the ion m/e 43 was used for detection of acetaldehyde. The calculations were made by means of calibration curves as in the case of aldehydes.

c. Ketones and Butyrolactone

The chromatographic separation was performed on the Carbowack C column. The ions m/e 42 and m/e 43 were used for detection of the compounds. The calculations were performed as described above.

d. Formaldehyde

The chromatographic separation was performed on Porapak T column. The ion m/e 30 was used for detection of formaldehyde. The calculations were made as described above.

RESULTS

To ensure as complete a separation of the compounds evolved during thermo-oxidation of LDPE as possible, four different columns were used. The 6% OS-138 column has a good ability to separate the majority of the products formed. Carbowack C column gives the best results for separation of the ketones, while Fluorad FC-431 column is most advantageous for separation of acids. The results of identification of the individual compounds are summarized in Table I. Gas chromatograms of the products of thermo-oxidation of LDPE on three columns are illustrated in Figures 3, 4, and 5.

Altogether 44 products representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, and cyclic esters were found. Among these products 10 compounds not described earlier were detected. To our knowledge, no mention has been made in the literature about formation from thermo-oxidative degradation of PE of the following volatile products: cyclopropane, furane, tetrahydrofuran (THF), isobutanal, methyl vinyl ketone, isovaleric acid, hydroxyvaleric acid, crotonic acid, caproic acid, and two lactones: valerolactone and butyrolactone. Most of these products are formed in low amounts, except of butyrolactone. The oxygen-containing compounds constitute an absolute majority, and the hydrocarbons, a minority of products detected during thermo-oxidation of LDPE. The results of the quantitative measurements of some volatile oxygen-containing products are given in Table II. The most abundant products formed are C_1 and C_2 acids and aldehydes.

DISCUSSION

Since our results are obtained at temperatures intermediate to those published in the literature, we consider it pertinent to discuss briefly the literature, for comparison with the results, concerning the volatile products reported here.

The thermo-oxidative degradation of LDPE and high density polyethylene (HDPE) samples (0.2 g) at 150°C in oxygen was studied by Matveeva et al.¹

TABLE I
Products of Polyethylene Thermo-oxidation

No.	Compound	Peak No. on Column			Identification	
		OS-138	Carbopack C	Fluorade FC-431	GC	MS
1.	Carbon dioxide	2		1	a	b
2.	Water	5		5	a	b
3.	Ethene	3			a	b
4.	Propene	7		2	a	
5.	Propane	7			a	
6.	Cyclopropane ^d	8				c
7.	Butene	11	6		a	
8.	Butane	11	8		a	
9.	Pentene	14			a	
10.	Pentane	14	15		a	
11.	Hexene	18			a	
12.	Hexane	18			a	
13.	Heptene	22			a	
14.	Heptane	22			a	
15.	Octene	26			a	
16.	Octane	26			a	
17.	Methanol	9			a	b
18.	Ethanol	13			a	b
19.	Furan ^d		9			c
20.	Tetrahydrofuran ^d		18			c
21.	Formaldehyde	6	1	6	a	b
22.	Acetaldehyde	10	2	3	a	b
23.	Propanal	15	4		a	b
24.	Acrolein	15			a	b
25.	Butanal	19	12		a	b
26.	Isobutanal ^d	19		8		c
27.	Pentanal	23			a	b
28.	Acetone	16	7		a	b
29.	Methyl vinyl ^d ketone		14		a	b
30.	Methyl ethyl ketone		13	9	a	b
31.	2-Pentanone		19	10		c
32.	2-Hexanone		27	13		c
33.	2-Heptanone	29				c
34.	Formic acid	12		14	a	b
35.	Acetic acid	17	16	15	a	b
36.	Propionic acid	20		17	a	b
37.	Acrylic acid	20		18	a	b
38.	Butyric acid	24		19	a	b
39.	Isovaleric acid ^d	28				c
40.	Hydroxyvaleric ^d acid		36			c
41.	Crotonic acid	25			a	b
42.	Caproic acid ^d			24		c
43.	Butyrolactone ^d		22		a	b
44.	Valerolactone ^d		26			c

^a According to retention time.

^b According to mass spectra of individual compounds.

^c According to mass spectra compared with Ref. 10.

^d Compounds which are identified probably for the first time.

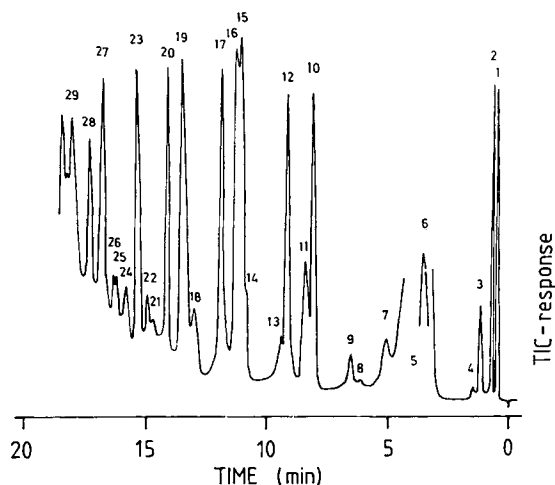


Fig. 3. Gas chromatography analysis of products of thermo-oxidation of LDPE on OS-138 column.

They found water to be the most abundant product of oxidation. Among the organic components, acids were found to be the most predominant, followed by formaldehyde and acetaldehyde. The aldehydes constitute about 30% of the total amount of acids. Acids were formed to a greater extent in the case of HDPE than for LDPE.

Bevilacqua et al.² were first to observe the formation of formic and acetic acids at thermo-oxidation of PE at 150°C. They came to the conclusion that the yield of acids depends on temperature and the crystallinity of the samples.

The thermo-oxidation of PE at 150°C and 160°C in oxygen atmosphere was studied by Barabás et al.³ By means of GC 15 oxidation products were identified.

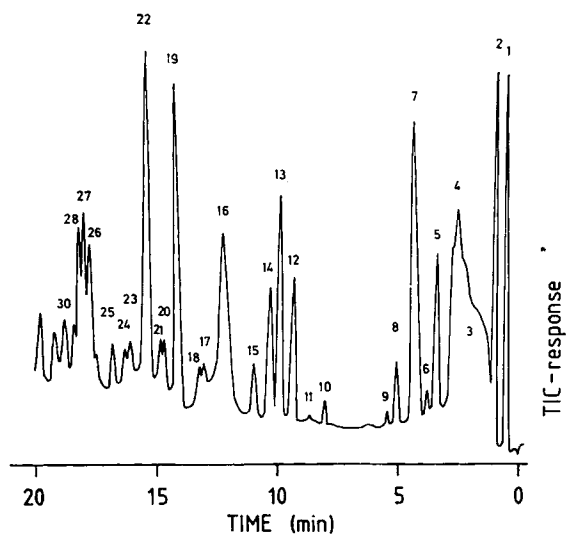


Fig. 4. Gas chromatography analysis of products of thermo-oxidation of LDPE on Carbo-pack C column.

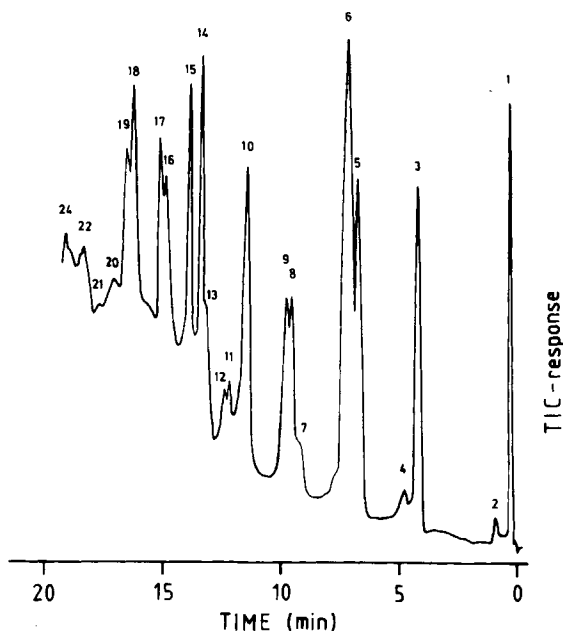


Fig. 5. Gas chromatography analysis of products of thermo-oxidation of LDPE on Fluorade FC-431 column.

Among the organic compounds found the predominant component was acetaldehyde, the amount of which was much higher than of any other product during the investigated time of degradation. A considerable amount of ethylene, propanal, butanal and low-molecular-weight alcohols were also detected.

The products formed during the thermo-oxidation of PE (72 h, 20 g of polymer) in the temperature range 75–200°C at oxygen concentration levels of 0–100% were studied with GC by Spore and Bethea.⁴ At 200°C and 33% of oxygen, 10 oxygen-containing compounds were found. The principal constituents were acetaldehyde (160 ppm), ethanol (260 ppm), and 2-pentanone (110 ppm).

The evolution of fatty acids, acrolein, and formaldehyde during smouldering combustion of PE was studied by Morikawa.⁵ He has found that the maximum yield of these volatiles was obtained at 300–400°C. At 350°C during 30 min of heating the yield of formaldehyde was about 78,000 ppm, acetic acid, 9500 ppm, formic acid, 8700 ppm, propionic acid, 2300 ppm, and acrolein, 16,500 ppm.

Michal and co-workers⁶ studied the products formed during thermo-oxidation of PE at 350°C in air. The main components found were C₃–C₁₅ aldehydes, representing 48.8% of the chromatographic area; oxygen-containing products in next abundance were ketones (2.8%). Epoxy compounds and ethanol were also identified. The remains were hydrocarbons, predominatingly olefines.

Thermo-oxidation of PE at 700–1000°C apart from carbon oxides and water leads to the formation of short chain linear hydrocarbons C₁–C₁₆. No organic oxygen-containing products were found in that research.⁷

In the present work, at temperatures 264–289°C, intermediate to those above, significant differences in thermo-oxidative degradation of PE were noticed. Ten additional volatile compounds were detected (see Table I). These products have not been previously mentioned in the literature. The quantitative measurements

TABLE II
Polyethylene Degradation Product Concentrations,^a $\mu\text{g/g}$ Polymer (ppm)

Compound	Temperature, °C			
	264	274	280	289
Aldehydes:				
Formaldehyde	900	1320	1780	2380
Acetaldehyde	1370	1770	1950	2400
Propanal	270		370	440
Acrolein	230		280	370
Butanal			700	
Pentanal			540	
Ketones:				
Acetone			250	
Methyl ethyl ketone			320	
Methyl vinyl ketone			30	
2-Pentanone			290	
Acids:				
Formic	2440	2980	3450	4120
Acetic	870	1200	1400	1760
Propionic		660	700	780
Acrylic		120	180	340
Butyric	85	205	230	300
Lactones:				
Butyrolactone			290	

^a Mean values for at least three experiments; the relative deviation is about $\pm 15\%$.

of the major products formed during oxidation at 264–289°C (Table II) give evidence that the main components among the degradation products are formic acid followed by formaldehyde, acetaldehyde, and acetic acid. The remainder of the products quantified are formed in amounts 5–20 times less than formic acid, except for the minor product methyl vinyl ketone.

According to Barabás et al.³ and Spore and Bethea⁴ acetaldehyde was found to be the principal product of thermo-oxidation of PE at 150°C and 160°C. Barabás et al.³ have also shown that the kinetic curve of acetaldehyde evolution is very similar to that of oxygen absorption by PE. Acetaldehyde, according to that work,³ was present in an amount exceeding that of any other component by nearly one order of magnitude. Morikawa,⁵ who worked at essentially higher temperature (300–400°C), has found that the main oxidation product was also an aldehyde, although formaldehyde. In our study we have found formic acid to be the main oxidation product. It is formed in amounts almost twice as much as acetaldehyde.

The discrepancies in the results obtained by different authors might likely arise from different experimental conditions (temperature and atmosphere) and from varying gas chromatographic conditions, e.g., using columns that are not proper, for separation of acids.

The effect of oxygen content and the effect of the temperature on the formation of different volatile products during thermo-oxidation of PE is illustrated by the following examples. Spore and Bethea⁴ have shown that the increase in oxygen content from 33 vol % to 100 vol % at 200°C results in a fourfold increase of the yield of formaldehyde and a sevenfold increase of the yield of acetaldehyde.

The effect of the temperature of LDPE oxidation during 4 min on the yield of the four most abundant products detected in our study is shown in Figure 6. As can be seen, formaldehyde formation is more sensitive to the rise of the oxidation temperature than acetaldehyde and the acids in our experimental conditions.

Degradation Reaction Mechanisms

The mechanism of thermal oxidation of hydrocarbons in the absence of additives could be described by well-known sequences of reactions presented in the following:

Scheme I

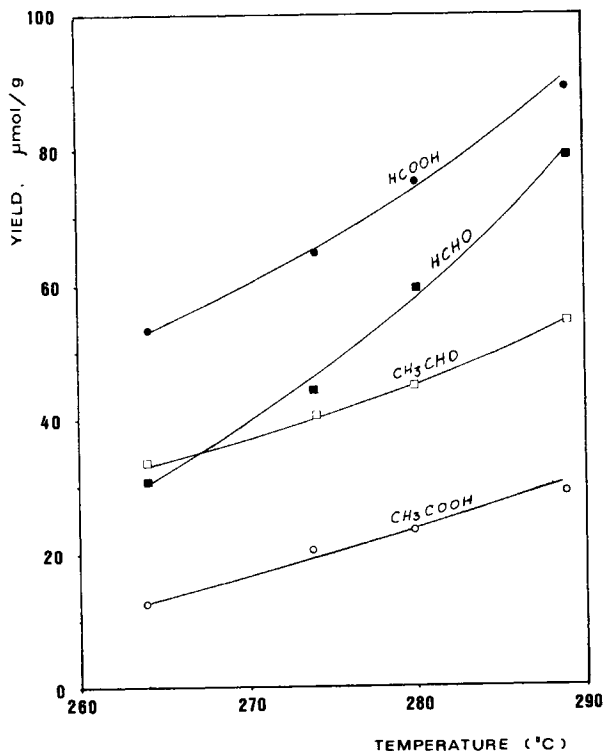
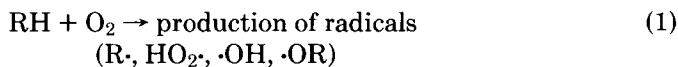
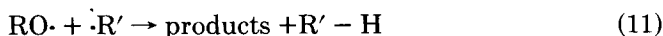
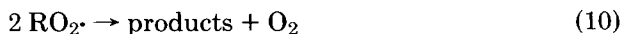
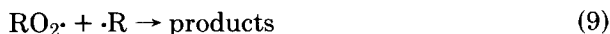


Fig. 6. The effect of temperature on the yields of some aldehydes and acids formed during oxidation of LDPE.



where $\cdot R'$ = any radical formed.

The first step of thermal oxidation is the formation of free radicals, the so-called primary initiation reaction, which can generally be represented by reaction (1). The reactions (2)–(5) represent propagation steps. Reaction (2) is very rapid, having an activation energy (E) of about zero value.¹² Reaction (3) is less rapid; the formation of hydroperoxide can proceed both by inter- and intramolecular hydrogen abstraction. When secondary and tertiary peroxides are involved, E is about 10.5 kcal/mol¹² for intermolecular reaction. The intramolecular hydrogen abstraction implies a ring transition state, the value of E varies in this case between 11 and 37 kcal/mol,¹² depending on the number of carbon atoms in the ring transition state. Reaction (5) for secondary and tertiary alkoxy radicals has an E value of about 3–11 kcal/mol.¹² Reactions (6) and (7) account for an initiation step. Reaction (6) for secondary and tertiary alkoxy radicals has an E value of about 44 kcal/mol.¹³ The reactions (8)–(11) are termination steps, and are generally very fast. The value of E for these reactions is about 3 kcal/mol.¹⁴ However, in the presence of oxygen (<100 torr) steps (8) and (9) may be neglected.¹⁴ Reaction (11) is a termination step, involving alkoxy radicals considered to be of importance in the thermo-oxidative degradation of PE under the conditions described.⁹ At high oxidation temperatures of hydrocarbons, formation and decomposition of peroxides and hydroperoxides can be expected to proceed very rapidly, thus resulting in formation of alkoxy radicals. The oxidized hydrocarbon fragments, as well as the various functional groups within the polymer, are formed in reactions of alkoxy radicals, resulting from the decomposition of hydroperoxides.¹⁵

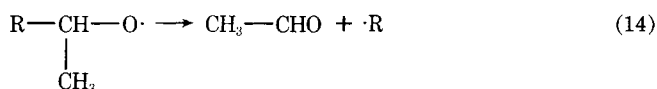
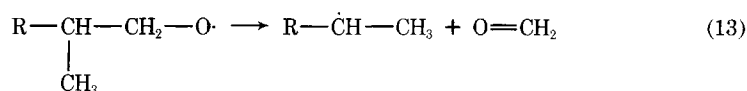
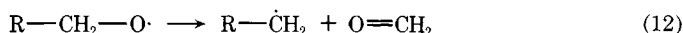
Before discussing the results, it should be stated that the formation of oxidized volatiles in the thermal degradation sampling system probably proceeds in two different conditions. Partially on and under the surface of the melted polymer, with restricted access of oxygen, and partially in the gas phase, rich with oxygen, by oxidation of fragments of decomposed polymer, volatile at the experimental conditions. This situation, which is quite usual during industrial processing, complicates the interpretation of the experimental results.

The destruction of the polymer, which occurs in the melt, is accompanied by chain scissions. This contributes to the formation of volatile, partially oxidized fragments of hydrocarbon. The volatiles are oxidized further in the gas phase rich with oxygen. The gas phase oxidation contributes probably in a high degree to the formation of short chain oxidized molecules. It should also be kept in mind that the volatiles escaping the polymer melt, which is kept at a rather high temperature (264–289°C), are cooled in a 200-mm-long transfer section, kept at 125°C, before reaching the glass trap. Thus the oxidation in the gas phase is performed in conditions of a certain temperature gradient.

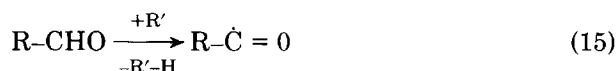
The most probable paths of formation of different classes of organic products during thermal oxidation of LDPE in the temperature range of 284–355°C were discussed thoroughly by Holmström and Sörvik.⁹ The reactions were considered

to account for the formation of aldehydes, ketones, alcohols, THF derivatives, and vinyl and vinylene groups within the polymer melt. However, these reactions are not completely adequate to explain some results found in our study, e.g., the high yield of C₁ and C₂ aldehydes and acids. Among the organic products found, the most abundant is formic acid, which is followed in abundance by formaldehyde, acetaldehyde, and acetic acid, respectively.

High concentrations of alkoxy radicals in the gas phase during thermo-oxidation of PE at 350°C have been reported.¹⁶ An alkoxy radical may react as follows:



Reaction (12) and reaction (13)¹⁴ contribute to formation of formaldehyde, while reaction (14)¹⁴ favors formation of acetaldehyde. Due to their labile hydrogen, the aldehydes formed are considered to undergo a rapid hydrogen abstraction and subsequent loss of carbon monoxide at temperatures about 264–289°C, reactions (15) and (16):



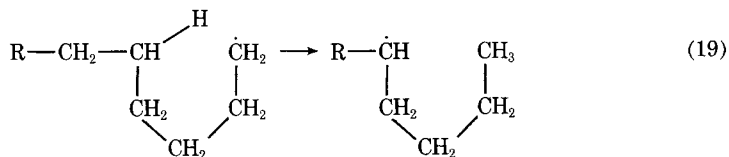
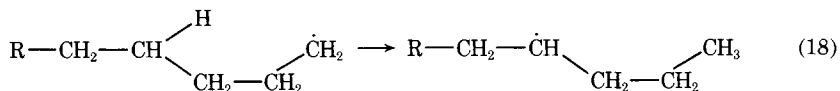
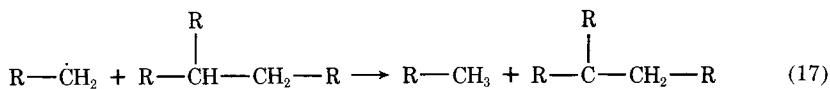
where R' is any radical present



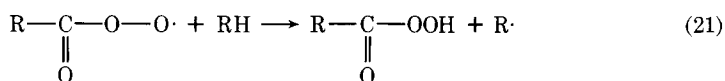
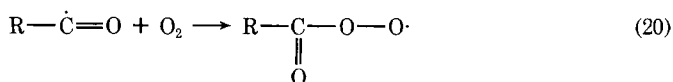
Thus it can be presumed that formaldehyde and acetaldehyde found are formed in the gas phase oxidation of volatile hydrocarbon fragments, rather than in the polymer melt. An alternative path for C₁–C₂ aldehyde formation in the gas phase oxidation may well involve methyl (methoxy) and ethyl (ethoxy) radicals. These radicals might come from gas-phase oxidation of escaped hydrocarbons or longer chain oxygen-compounds. Spore and Bethea⁴ have shown that the rise of oxidation temperature and oxygen content during PE oxidation has a profound effect on the yield of methane. Methyl radicals, which are the precursors of methane, should in an oxygen-rich atmosphere form methyl peroxides and eventually methoxy radicals. The latter may serve as a source for formation of formaldehyde and formic acid.¹⁷

The rather high amounts of methyl end groups essential to account for formation of short chain aldehydes, acids, and ketones could have been generated within the polymer melt in oxygen starved conditions. The methyl groups could have been formed in the course of intermolecular [reaction (17)] and intramolecular (back-biting) reactions^{18–22} (18) and (19) of hydrogen abstraction by a primary radical. The value of *E* for hydrogen abstraction by a primary radical

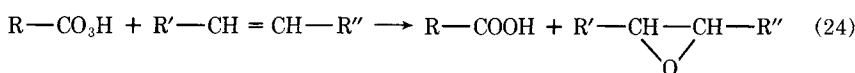
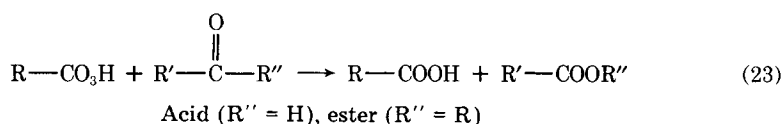
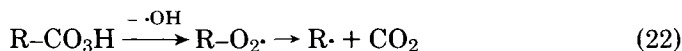
is about 10 kcal/mol²³ both for inter- and intramolecular reactions:



The aldehydes present in the gas phase can easily lose a hydrogen atom in reactions of chain transfer (15), thus forming acyl radicals. Depending on oxygen pressure, the acyl radicals either decarbonylate [reaction (16)] or form acylperoxy radicals [reaction (20)], which attack hydrocarbon fragments with the formation of peracids [reaction (21)]:



Peracids can further participate in reactions as follows:



The peracids formed in the polymer melt would most probably decompose, according to reaction (22). The peracids formed in the gas phase can oxidize ketones to esters, leaving acids, or can oxidize aldehydes to acids. Vinylene compounds in the gas phase can be converted to epoxides, leaving acids. No epoxides or acyclic esters were detected by the GC/MS analysis. However, rather high amounts of acids were found. It can be presumed that the C₁ and C₂ aldehydes detected represent only a part of these products formed, which escaped further transformations. The other part of the aldehydes formed in the gas phase have presumably been involved in reactions (15) and (20) giving peracids, and thus enabling formation of acids. Formation of acids and 2-ketones can also proceed

Altogether 44 compounds representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters, and hydroxycarboxylic acids were identified.

Sixteen oxygen-containing products were quantified. The fatty acids are the principal organic products of thermo-oxidation of LDPE, followed by aldehydes and ketones. The most abundant product formed is formic acid.

This work is part of research program of thermal and thermo-oxidative degradation of polymers supported by the Swedish Work Environment Fund. The authors are grateful to Dr. John C. MacDonald for valuable comments on the manuscript.

References

1. E. M. Matveeva, S. S. Khinkis, A. I. Tsevetkova, and V. A. Balandina, *Plast. Massy*, **1**, 2 (1963).
2. E. M. Bevilacqua, E. S. English, and J. S. Gall, *J. Appl. Polym. Sci.*, **8**, 1691 (1964).
3. K. Barabás, M. Iring, T. Kelen, and F. Tüdös, *J. Polym. Sci., C*, **57**, 65 (1976).
4. R. L. Spore and R. M. Bethea, *Ind. Chem. Prod. Res. Dev.*, **11**, 36 (1972).
5. T. Morikawa, *J. Combust. Toxicol.*, **3**, 135 (1976).
6. J. Michal, J. Mitera, and S. Tardon, *Fire Mater.*, **1**, 160 (1976).
7. E. A. Boettner, G. L. Ball, and B. Weiss, Combustion products from the incineration of plastics, Report, No. EPA-670/2-73-049, University of Michigan, Ann Arbor, Michigan 48104.
8. A. Holmström and E. Sörvik, *J. Appl. Polym. Sci.*, **18**, 761 (1974).
9. A. Holmström and E. Sörvik, *J. Appl. Polym. Sci.*, **18**, 3153 (1974).
10. A. Cornu and R. Massot, *Compilation of Mass Spectral Data*, 2nd ed., Heyden, London, 1975.
11. W. W. Blaser and W. R. Kracht, *J. Chromatogr. Sci.*, **16**, 111 (1978).
12. A. Fish, in *Organic Peroxides*, D. Swern, Ed., Wiley-Interscience, New York, 1970, Vol. 1, p. 141.
13. S. W. Benson and R. Shaw, in *Organic Peroxides*, D. Swern, Ed., Wiley-Interscience, New York, 1970, Vol. 1, p. 105.
14. L. Reich and S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971, p. 7.
15. T. Kelen, M. Iring and F. Tüdös, *Eur. Polym. J.*, **12**, 35 (1976).
16. J. Wartiovaara-Tuompo, F. Sundholm, and P. Pfäffli, Chemistry Days in Helsinki, November 14-16, 1979.
17. F. R. Mayo, *Am. Chem. Soc. Div. Petrol. Chem. Prep.*, **19**(4), 627 (1974).
18. N. Grassie, *Chemistry of High Polymer Degradation Processes*, Butterworths, London, 1956, p. 68.
19. W. J. Bailey and C. L. Liotta, *ACS Polym. Prep.*, **5**(2), 333 (1964).
20. W. J. Bailey and L. J. Baccei, *ACS Polym. Prep.*, **12**(2), 313 (1971).
21. Y. Tsuchiya and K. Sumi, *J. Polym. Sci., A-1*, **6**, 415 (1968); *J. Polym. Sci. B*, **6**, 357 (1968).
22. J. van Schooten and J. K. Evenhuis, *Polymer*, **6**, 343, 561 (1965).
23. J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
24. D. R. Sharp, L. W. Patton, and S. E. Whitcomb, *J. Am. Chem. Soc.*, **73**, 5600 (1951).

Received December 6, 1980

Accepted April 23, 1981