

Identification of Volatile Compounds Resulting from the Thermal Oxidation of Polyethylene

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SYNOPSIS

The migration of compounds from polymer-based packaging may impart undesirable odors to foods. We, therefore, undertook a study of the volatile compounds produced during the heating of polyethylene (PE) in the presence of excess O₂ at temperatures of 150–350°C and for heating times of 5–15 min. Eighty-four volatile compounds in the range of C₅–C₂₃ were identified by gas chromatography mass spectrometry. The major products were aliphatic hydrocarbons, aldehydes, ketones, and olefins. Changes in temperature and heating times affected the amount and type of compounds produced, with hexanal being found in the largest amount and 300°C resulting in the greatest quantity of volatile compounds. At 350°C, greater amounts and numbers of low-boiling and fewer high-boiling compounds were formed. Only small amounts of volatiles were produced at 150°C. Many of the compounds identified have been reported to have odor and/or toxicological significance. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

High-temperature-high-shear processing of polyolefins into food-packaging materials can cause thermal oxidation of the polymer, resulting in scission, cross-linking, and/or oxidation of macromolecules. These changes affect physicomechanical properties, stability during use, and suitability for some applications. The resulting low molecular weight residual products can transfer to foods with potential toxicity and/or deleterious food-quality effects. In particular, the compounds formed during thermooxidative degradation can impart undesirable odors and flavors. Packaging components that migrate to foods also become indirect food additives, and in the United States, they are regulated by the Food and Drug Administration.

Processing polyethylene (PE) into packaging materials often takes place between 200 and 370°C. There have been investigations into the structure of the volatiles formed below 200°C,^{1–5} and under pyrolysis conditions (i.e., above 350°C^{6–11}), but

fewer in the temperature range encountered in processing.^{12–16} Oxygen-containing low molecular weight products such as aldehydes, ketones, and acids, including toxic compounds such as formaldehyde, formic acid, and acrolein, have been identified. With the exception of Hoff and Jacobsson,¹⁶ no attempt to exhaustively identify the volatile compounds resulting from the thermooxidation of PE at normal processing temperatures has been made. Hoff and Jacobsson¹⁶ trapped the volatiles produced by PE thermooxidative degradation over the temperature range of 264–289°C. Forty-four compounds, including hydrocarbons, alcohols, aldehydes, ketones, acids, and cyclic ethers, were identified by gas chromatography-mass spectrometry (GC-MS). Their system was designed such that very low molecular weight compounds would be efficiently detected, perhaps at the expense of mid- to higher-boiling components. For example, the most abundant compounds were formic acid, formaldehyde, acetaldehyde, and acetic acid.

The nature and amount of compounds identified during thermooxidative degradation depend on polymer morphology and composition, degradation conditions, and conditions of analysis. The objectives of our work were to identify and quantify the

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volatile compounds formed from the thermooxidation of PE down to a minimum concentration of approximately 2 μg of volatile compound per gram of PE at temperatures similar to those used in polymer processing. Compounds occurring below this level would probably not be toxicologically or organoleptically significant. We chose the conditions of the analysis to focus on oxygenated compounds in the $\text{C}_4\text{-C}_{22}$ range because these compounds are most likely to have significant odor. We also wanted to determine the effects of time and temperature on the amounts and distribution of formed compounds.

EXPERIMENTAL

Materials

PE with approximate MW of 50,000; density, 0.92 g/cm^3 ; $n^{25/D}$, 1.51; and melt index, 0.8, and soluble (above 60°C) in aliphatic, cycloaliphatic, and aro-

matic hydrocarbons was acquired from Scientific Polymer Products (Ontario, NY). The all-glass device used to thermally oxidize the PE and to trap the volatiles was a modification of those previously reported^{9,10,16} and consisted of a heated sample tube and two traps in a series (Fig. 1). The heated tube was continuously purged by 20 mL/min of air. The air was passed through a trap containing activated charcoal to absorb any potential contaminants prior to entering the apparatus. The degradation tube was a 50 mL glass impinger (Wheaton, Millville, NJ) connected to two glass vapor traps (50 mL, Wheaton) by 1 cm i.d. glass tubing kept at elevated temperature by heating tape. The traps were cooled in liquid N_2 . The second trap was linked to a water trap to compensate for the vacuum created by the low temperature.

Samples of PE (0.5 g) were dispersed in approximately 0.3 g of glass wool (to increase surface area) and placed in the glass vessel. The vessel was then placed inside the heated oven. Volatiles were swept

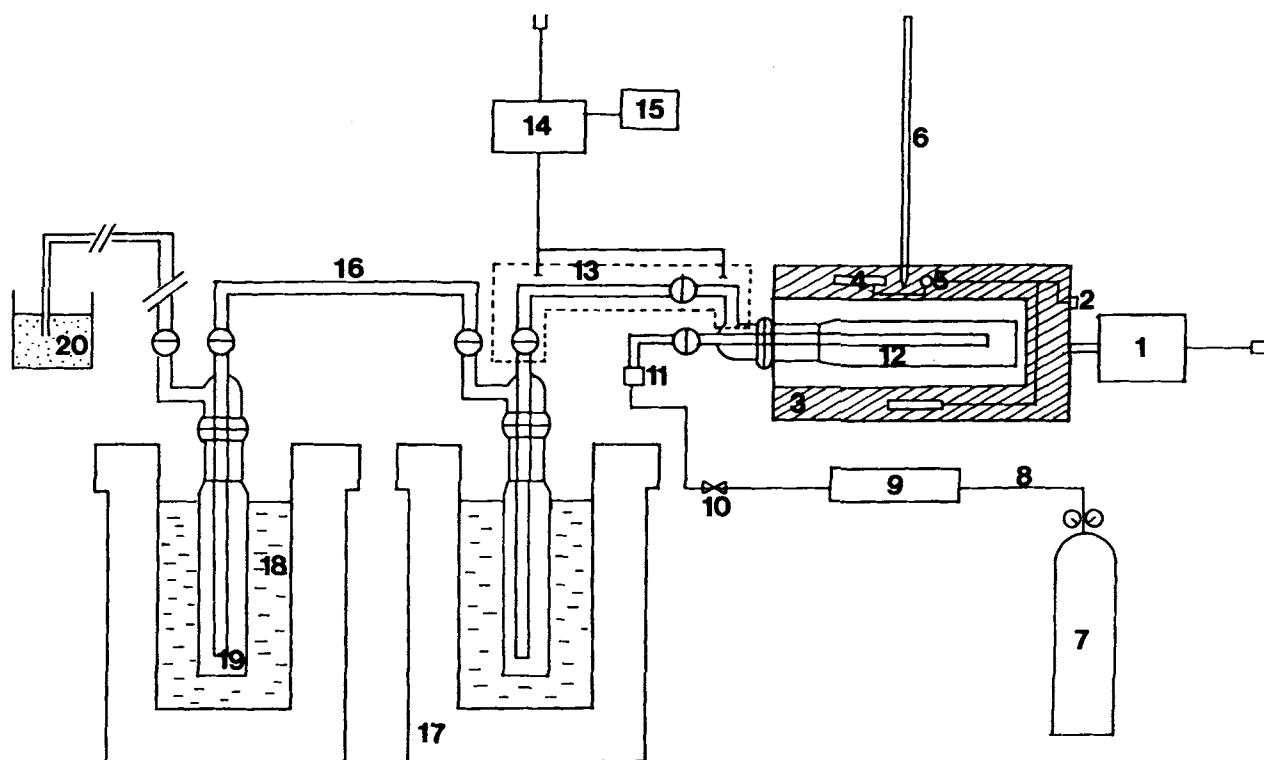


Figure 1 Degradation/collection system for the isolation of volatiles: (1) control box for oven temperature; (2) temperature adjusting screw of CAL-STAT; (3) aluminum block-furnace with rock wool insulator; (4) cartridge heaters; (5) Vulcan CAL-STAT thermostat; (6) thermometer (0–400°C); (7) compressed air bottle; (8) copper tubing; (9) metal trap with activated charcoal; (10) control valve; (11) brass-to-glass joint with graphite ferrule; (12) glass degradation tube; (13) heating tape; (14) variable autotransformer; (15) digital thermometer; (16) glass tubing; (17) Dewar flasks; (18) liquid nitrogen baths; (19) glass traps; (20) water trap.

out by the air and condensed in the traps. Volatiles were extracted from the traps by washing with 4 mL of ultrapure Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane, $T_b = 47.7^\circ\text{C}$). Solutions were stored for later analysis at 5°C in sealed 10 mL glass vials. When necessary for further analysis by GC-MS, samples were concentrated 5 \times , 10 \times , and 100 \times by evaporation under a slow stream of N_2 . PE samples were heated at 150, 200, 250, 300, and 350°C for 15 min and at 250°C for 5, 10, 15, 20, 25, and 30 min.

Gas Chromatography/Mass Spectrometry

Trapped compounds were identified by full-scan electron impact GC-MS using a splitless injection of $1\ \mu\text{L}$ into a Hewlett-Packard 5890 gas chromatograph coupled to a 5970 mass selective detector and equipped with a $0.32\ \text{mm} \times 25\ \text{m}$ fused silica capillary column coated with cross-linked methyl silicone. GC

temperatures were 35°C at 3 min hold; $4^\circ\text{C}/\text{min}$ to 225°C ; injector and ion source at 200°C ; and carrier gas, helium, at $2\ \text{mL}/\text{min}$. Electron multiplier voltage was 2000 eV. Compounds were identified by comparison of their mass spectra with the NBS Wiley Data Base and, in some cases, by comparison to authentic compounds.

Gas Chromatography/Flame Ionization Detector

Quantitative analysis of volatiles was performed by injection of $1\ \mu\text{L}$ into a Hewlett-Packard 5790 A Series gas chromatograph equipped with a $0.32\ \text{mm} \times 12\ \text{m}$ fused silica capillary column coated with 100% dimethyl polysiloxane and with flame ionization detection (FID). GC conditions were injector at 200°C ; detector at 250°C ; oven temperatures: 30°C at 3 min hold, $4^\circ\text{C}/\text{min}$ to 225°C , hold for 10 min; and carrier gas, N_2 , $1\ \text{mL}/\text{min}$. Responses were

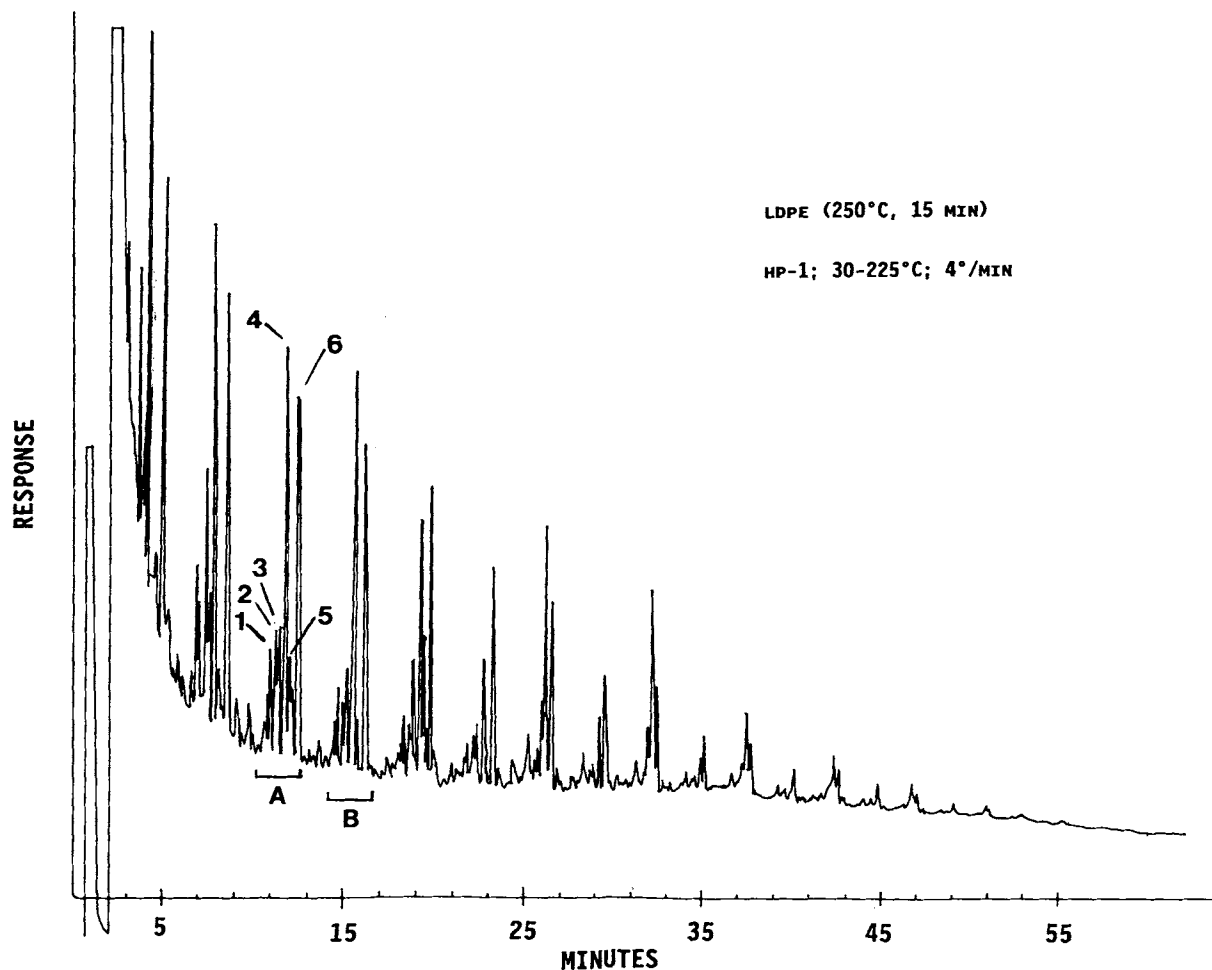


Figure 2 GC/FID chromatogram of the volatiles condensed from an LDPE sample heated at 250°C for 15 min.

Table I Compounds Identified by GC-MS from the Thermal Oxidation of PE: Variation in Volatile Composition with Temperature (Heating Time 15 Min) and Heating Time (Temperature 250°C)

Compound	Index	$\mu\text{g/g PE}^a$ ($^{\circ}\text{C}$)					$\mu\text{g/g PE}^b$ (min)					
		150	200	250	300	350	5	10	15	20	25	30
Heptane	700			66	80	82		22	66	48	66	57
3-Hexanone	761			25	35	31		9	25	22	31	26
2-Hexanone	765			46	97	69		13	46	35	53	42
Hexanal	774			177	193	90	< 2 ^d	54	177	158	224	200
Octane	800			85	94	66	< 2 ^d	27	85	67	90	83
2-Hexenal	826			8	12	17		2	8	7	10	10
1-Hexenal	857			26	26	50		6	26	18	33	28
3-Heptanone	865			51	66	51	< 2 ^d	18	51	44	65	58
2-Heptanone	868			40	77	59		10	40	30	40	35
Heptanal	878			100	114	64	2	28	100	90	126	116
1-Nonene	888			23	44	70		6	23	16	21	17
Nonane	900			121	112	51	< 2 ^d	25	121	76	113	103
T-Heptanol	955			23	20	51		6	23	19	27	25
3-Octanone	962			27	32	27		7	27	25	31	28
2-Octanone	965			32	63	49		8	32	25	36	33
Octanal	975	< 2 ^d	2	107	106	46	2	32	107	97	136	130
1-Decene	988	2	3	48	45	51	3	10	48	26	34	31
Decane	1000	< 2 ^d	< 2 ^d	93	85	53	< 2 ^d	26	93	64	92	85
1-Octanol	1059			22	28	34		4	22	16	22	21
3-Nonanone	1064			18	20	19		4	18	18	22	21
2-Nonanone	1068			27	45	29		6	27	22	30	27
Nonanal	1081			97	91	42	1	23	97	82	110	105
1-Undecene	1088			14	13	24		3	14	10	13	14
Undecane	1100			85	69	41	< 2 ^d	22	85	62	79	82
2-Nonenal	1134			11	8	6		2	11	7	7	12
1-Nonanol	1159			18	22	18		3	18	12	17	17
3-Decanone	1168			16	23	14		3	16	13	18	20
2-Decanone	1172			33	38	18		6	33	20	26	24
Decanal	1185	6	11	70	70	24	8	26	70	63	83	79
1-Dodecene	1189	14	25	46	36	21	16	30	46	34	43	39
Dodecane	1200	3	6	81	60	24	4	23	81	57	79	73
3-Undecanone	1269			12	14	9		2	12	11	12	12
2-Undecanone	1274			21	28	13		5	21	15	18	18
Undecanal	1286			36	47	14		11	36	37	46	48
1-Tridecene	1289											
Tridecane	1300			62	46	17	< 2 ^d	13	62	40	55	51
3-Dodecanone	1370			8	8	< 2 ^d		< 2 ^d	8	5	6	7
2-Dodecanone	1375			14	18	6		< 2 ^d	14	9	10	12
Dodecanal	1383	5	14	26	16	4	7	17	26	18	19	18
1-Tetradecene	1389											
Tetradecene (7) ^c	1392	15	46	90	76	22	21	48	90	67	70	72
Tetradecene (7) ^c	1395											
Tetradecane	1400	2	6	53	39	11	3	16	53	36	44	44
Tetradecene (5) ^c	1412	< 2 ^d	3	6	6	< 2 ^d	1	3	6	4	4	4
3-Tridecanone	1472			3	9			< 2 ^d	3	3	3	3
2-Tridecanone	1476			7	12	4		< 2 ^d	7	6	5	6
Tridecanal												
Pentadecene	1490	5	18	18	27	10	6	16	18	26	22	27
Pentadecane	1500			34	23	7	< 2 ^d	6	34	19	22	26
3-Tetradecanone	1573			3	5	2			3	2	2	4
2-Tetradecanone	1578			5	8	< 2 ^d			5	3	2	6
Tetradecanal	1584	< 2 ^d	4	16	11	2	2	10	16	11	10	12

Table I (continued)

Compound	Index	$\mu\text{g/g PE}^a$ ($^{\circ}\text{C}$)					$\mu\text{g/g PE}^b$ (min)					
		150	200	250	300	350	5	10	15	20	25	30
1-Hexadecene	1590											
Hexadecene (7) ^c	1592	3	14	66	45	11	8	31	66	45	38	48
Hexadecene (7) ^c	1596											
Hexadecane	1600		< 2 ^d	25	19	6	< 2 ^d	6	25	18	18	24
Hexadecene	1613			4	2			2	4	2	2	2
Tridecanoic acid	1648			1	2				1			< 2 ^d
3-Pentadecanone	1675			1	2				1	< 2 ^d	< 2 ^d	2
2-Pentadecanone	1680			3	3				3	< 2 ^d	< 2 ^d	3
1-Heptadecene	1690											
Pentadecanal	1695			8	9	3		< 2 ^d	8	6	6	10
Heptadecane	1700			14	11	3		2	14	10	9	14
Tetradecanoic acid	1747				1							< 2 ^d
3-Hexadecanone	1777				< 2 ^d							< 2 ^d
2-Hexadecanone	1781				< 2 ^d							2
1-Octadecene	1790											
Octadecene (5) ^c	1797		4	29	24	3	5	13	29	21	15	26
Octadecane	1800											
Pentadecanoic acid	1845			12	10	< 2 ^d	< 2 ^d	< 2 ^d	12	8	7	13
3-Heptadecanone	1878				< 2 ^d							< 2 ^d
2-Heptadecanone	1883			3	6				3			5
Nonadecene	1891											2
Nonadecane	1900			12	14	< 2 ^d		< 2 ^d	12	9	6	14
Hexadecanoic acid	1944				3							2
Eicosane (3) ^c	1991			18	12			7	18	12	6	11
Eicosene (C20)	2000			10	11	< 2 ^d		< 2 ^d	10	6	6	13
Heptadecanoic acid	2044											
Heneicosane (C21)	2100			5	7	2		< 2 ^d	5	4	2	8
Octadecanoic acid	2142											
Docosane (C22)	2200			5	6	< 2 ^d		< 2 ^d	5	3	< 2 ^d	7
Tricosane (C23)	2300			3	4				3	2	< 2 ^d	5

^aHeating time: 15 min.

^bTemperature: 250 $^{\circ}\text{C}$.

^cMost probable location of the double bond.

^dLimit of detection = 2 $\mu\text{g/g PE}$.

recorded both by a Hewlett-Packard 3392 A integrator and a Fisher Recordall Series 5000 recorder. Compounds were identified by comparison of retention indices with those obtained by GC-MS and the quantity approximated by comparison of peak areas with the average of a series of C₇-C₁₈ *n*-hydrocarbons standards.

RESULTS AND DISCUSSION

No peaks were detected in analyses that included all components except polymer, indicating that all compounds came from thermooxidation of the PE. The chromatogram was complex with over 100 observable peaks (Fig. 2). Peaks were distributed in

symmetric groups with a change in retention index of approximately 100 between corresponding peaks from different groups. Adding a methylene unit to a molecule generally increases the retention index by 100.¹⁷ This suggested a homologous series of compounds. For example, in groups A and B (Fig. 2), the last large peak in A was identified as decane and the analogous peak in group B was undecane. In group A (Fig. 2), peak 1 was identified as 1-heptanol; peak 2, as 3-octanone; peak 3, as 2-octanone; peak 4, as octanal; peak 5, as 1-decene; and peak 6, as decane. This pattern (C_{*n*-1} 1-alkanol, C_{*n*} 3-alkanone, C_{*n*} 2-alkanone, C_{*n*} alkanal, C_{*n*+1} 1-alkene, C_{*n*+1} alkane) was repeated in all peak groupings in which there was a sufficient compound for positive GC-MS identification. This repetitive behavior

suggests multiple and parallel degradation reactions were taking place.

Eighty-four compounds were identified by comparing GC-MS spectra to standard spectra in the NBS Wiley database; matching probabilities were at least 80% and often as high as 99% (Table I). Data were correlated with the GC-FID responses for each detectable peak and the quantity of compound formed estimated. Retention indices (Kovats indices¹⁸), GC-MS and GC-FID retention times, and the μg compound formed per gram of polymer were calculated (Table I). The quantity of compound formed per gram of polymer was calculated assuming that the FID response factors would be the same for all compounds and equal to the average response of a mixed standard (1 $\mu\text{g}/\text{mL}$ each) of C_7 - C_{18} *n*-hydrocarbons run under identical conditions. These quantitative results are approximations since the FID detector responds proportionally to the amount of C, O, and H in the sample. However, response factors vary for different compounds. More accurate results would be obtained if all response factors were known. Correlation of GC-MS and GC-FID retention indices was good, based on the saturated hydrocarbon internal standards.

The structures obtained were consistent with the mechanism proposed by Holstrom and Sorvik¹⁵ for thermooxidative degradation of polyolefins (Fig. 3). Aldehydes and 2- and 3-ketones were the most abundant oxygen-containing products. They could be produced by transformation of alkoxy radicals (Fig. 3, reactions K-N). However, no ethers were identified, suggesting that reaction K is favored under our conditions to give aldehydes and hydrocarbons. Alcohols were found in lower quantities than were carbonyl products, further suggesting that reactions K and N (Fig. 3) were favored over L and M. High molecular weight carboxylic acids were present but in low amounts. No esters or cyclic compounds were identified.

The amounts of saturated hydrocarbons and carbonyl compounds produced were similar. Both compound classes could be formed by reactions K and M (Fig. 3). However, olefins and paraffins can also be formed in the absence of oxygen. Alkyl radicals can undergo depolymerization with intra- and intermolecular hydrogen abstraction followed by β -scission. Termination by combination or disproportionation leads to these hydrocarbons. A combination of thermal degradation (taking place in parts of the sample where diffusion of O_2 is low) and thermal oxidation (taking place in zones of high O_2 concentration) processes could account for the range of products detected.

Studies of PE degradation at temperatures below 200°C have reported only a few volatile compounds, with formic and acetic acids and aldehydes being the most abundant.¹⁻⁴ We did not detect these compounds, most likely because of differences in gas chromatographic conditions. We did identify 15 compounds as products from degradation at 150-200°C, including aldehydes, alkanes, and alkenes (Table I). The major products found in previous studies were water, CO, CO_2 , methane, and ethylene.¹⁹ Similar low molecular weight components were probably present in our condensed sample but not detected in the GC-FID chromatogram because of masking by the solvent peak or because of differences in chromatographic conditions.

Above 250°C, C_3 - C_{15} aldehydes, ketones, olefins, ethers, and alcohols have been identified.^{6,12,13,15,20} In the most extensive study published, Hoff and Jacobsson¹⁶ identified 44 hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, and cyclic esters from PE heated to 264-289°C. Their results are similar to ours for the C_4 - C_7 2-ketones and low molecular weight alkanes, alkenes, and aldehydes. They found more low molecular weight components, probably due to methodological differences. However, we found a considerably larger number of compounds in the range C_5 - C_{23} .

Effect of Temperature on Polyethylene Oxidation

As expected, heating the polymer for the same time (15 min) at temperatures between 150 and 350°C qualitatively and quantitatively influenced the results (Table I). At 150 and 200°C, only traces of paraffins, olefins, and aldehydes were detected. Compounds with an even number of carbons predominated, except for tridecanal and pentadecene. The amounts formed increased substantially at temperatures of 250°C or greater. Chromatograms were qualitatively similar but quantitatively increased with increasing temperature. At a given temperature, the amount of compound formed increased with volatility or decreasing retention index. Hexanal was the most abundant compound detected in each case. In general, larger amounts of product were obtained in the order of 250°C < 350°C < 300°C. At 350°C, fewer compounds with a large retention index were formed.

Effect of Time on Polyethylene Oxidation

Increasing the heating time from 5 to 30 min increased the amount of volatiles formed at 250°C (Table I). These heating times exceed processing

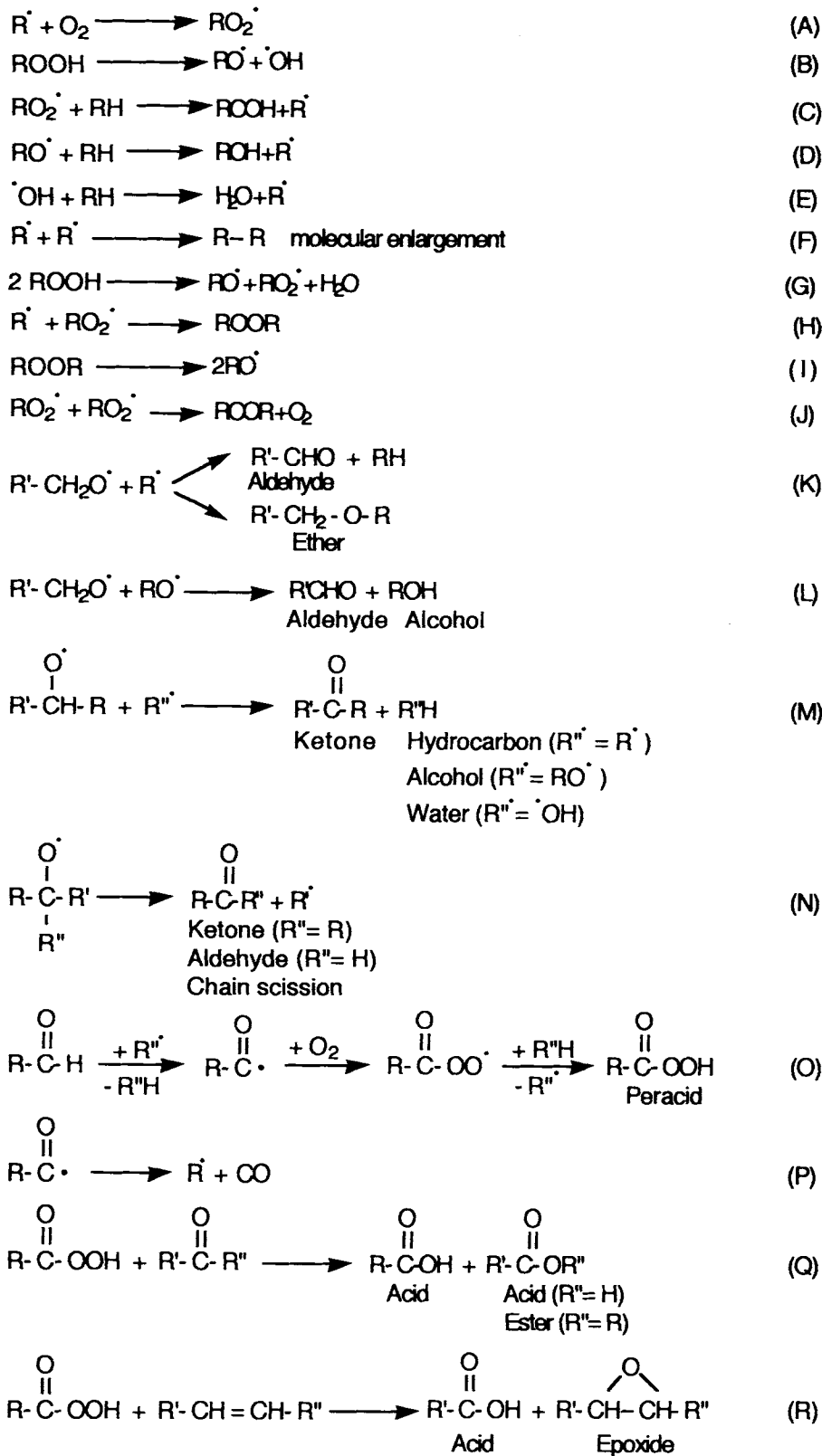


Figure 3 Proposed by mechanism of thermooxidative degradation of PE [15].

conditions but were used in order to collect sufficient trace volatiles for identification. Few compounds were detected when PE was heated for 5 min. This was probably due to insufficient time for the polymer to reach the oven temperature since time was recorded from the moment the degradation vessel was introduced into the oven. A significant change in the chromatogram was noticed for heating times over 10 min. Fewer higher molecular weight components were detected and larger amounts of low retention index products were formed. Hexanal was the most abundant product in each case. Butanal and pentanal were identified by GC-MS but could not be quantified by GC-FID due to interference by the solvent peak.

These data show that several compounds that possess undesirable odor characteristics are formed during the thermooxidation of PE in the temperature range used during package manufacture. We are currently studying the individual odor characteristics of these compounds and will report results in due course.

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Received February 18, 1992

Accepted February 25, 1992