SANDIA REPORT
SAND2013-1600
Unlimited Release
Printed February 2013

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Identification of Volatile Butyl Rubber Thermal-Oxidative Degradation Products by Cryofocusing Gas Chromatography/Mass Spectrometry (Cryo-GC/MS)

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Abstract

Chemical structure and physical properties of materials, such as polymers, can be altered as aging progresses, which may result in a material that is ineffective for its envisioned intent. Butyl rubber formulations, starting material, and additives were aged under thermal-oxidative conditions for up to 413 total days at up to 124 °C. Samples included: two formulations developed at Kansas City Plant (KCP) (#6 and #10), one commercially available formulation (#21), Laxness bromobutyl 2030 starting material, and two additives (polyethylene AC-617 and Vanax MBM). The low-molecular weight volatile thermal-oxidative degradation products that collected in the headspace over the samples were preconcentrated, separated, and detected using cryofocusing gas chromatography mass spectrometry (cryo-GC/MS). The majority of identified degradation species were alkanes, alkenes, alcohols, ketones, and aldehydes. Observations for Butyl #10 aged in an oxygen-18 enriched atmosphere ($^{18}O_2$) were used to verify when the source of oxygen in the applicable degradation products was from the gaseous environment rather than the polymeric mixture. For comparison purposes, Butyl #10 was also aged under non-oxidative thermal conditions using an argon atmosphere.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Donald R. Bradley for his assistance in sample preparation and aging. We would also like to thank Mark Wilson for providing the butyl rubber samples as developed by him at Kansas City Plant. Funding was provided by the Enhanced Surveillance Campaign (ESC).

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1. INTRODUCTION

Butyl rubber, also known as isobutylene isoprene rubber (IIR), is a synthetic copolymer rubber comprised of isobutylene (~98%) and minor amounts of isoprene (~2%), as depicted in Figure 1 [1]. The diene group of isoprene incorporates a double bond in the polymeric structure of butyl rubber that is then available as a crosslinking site for the polymeric chains (e.g., crosslink of sulfur vulcanized butyl rubber) [2]. The number of potential crosslinking sites can be controlled by varying the amount of isoprene introduced during synthesis [2], and we have shown a simplified structure for butyl rubber (Figure 1). These vulcanization reactions are slow due to the low levels of unsaturation in the polymeric backbone [3]. Butyl rubber has good flexibility, weathering and ozone resistance, vibration damping, aging stability, heat resistance, and biocompatibility [3, 4]. Uniquely, butyl rubber is also air tight and virtually gas impermeable [3, 4]. Halogenation of butyl rubbers with chlorine or bromine has allowed for the co-vulcanization of the polymer with other rubbers (e.g., natural, styrene-butadiene (SBR), and diene rubbers) [5], which has led to improvement in vulcanization rates, states of cure, and reversion resistance [3]. Though all halogenated butyl rubbers have similar properties, the bromine sites of bromobutyl rubber are more reactive than those from chlorine, resulting in faster curing times along with better adhesion to unsaturated rubbers [3]. Typical applications of butyl rubbers include: tubeless tire liners, inner tubes, biomedical joint replacements, curing bladders, protective chemical warfare gear, pharmaceutical stoppers, construction sealants, hoses, chewing gum, and O-rings [4, 5].

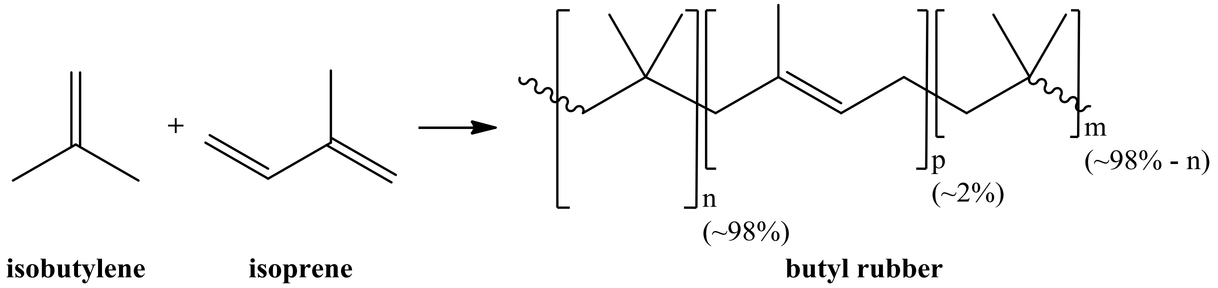


Figure 1. General formula for butyl rubber formation

Butyl rubber is an ideal candidate for O-ring seals due to its low permeation rates for gases, including potentially hazardous gaseous decomposition products, and ability to provide a system with an airtight seal. These characteristics are vital for high-reliability applications, such as weapon systems, where a loss in O-ring functionality or integrity would be detrimental. For many decades, several weapons systems have used O-rings made of butyl rubber as environmental seals. However, the O-rings were traditionally supplied by external vendors, which meant the DOE complex did not have control over the O-ring formulation. This became a problem, for example, when vendors changed their proprietary formulations without notice to their customers. Because the chemical and mechanical properties of the butyl rubber fundamentally depend upon the structural chemistry of the polymer, a change in formulation additives (e.g., carbon black, anti-oxidants, curing agents, *etc*.) or a lack of quality control could easily affect the physical and aging properties of the material and thus health of the stockpile. As a result, twenty candidate butyl rubber formulations were developed by Mark Wilson at Kansas City Plant (KCP) for a DOE complex-controlled butyl rubber formulation to be used in weapon related O-rings [6-8]. Two of these formulations (Butyl #6 and #10, arbitrarily named) provided the most promise and were selected by Sandia as candidates for aging studies [6], as well as the identification of volatile degradation species that may outgas into the weapon system, with potential detrimental effects on other WR materials.

To increase the butyl rubber knowledgebase, past reports regarding the limitations and degradation of butyl rubber were summarized by Dubey, *et al*. [9] for the following areas of research: thermal and thermal-oxidative conditions, mechanical stresses, catalytic reactions, chemical and electrochemical effects, radiation-induced changes, and alterations due to ozonolysis. Most of the structural studies were qualitative in nature and concluded that thermal-oxidative degradation of butyl rubber is mainly by chain scission, whereas halobutyl elastomers undergo cross-linking [10]. It was also shown that butyl rubber is more sensitive to light than it is changes in thermal-oxidative conditions and ozonolysis [9]. A study in 1993 [11] investigated the major thermal decomposition products of butyl elastomer by way of pyrolysis *via* cryogenically trapping the pyrostate and then analyzing it with gas chromatography (GC) coupled to either a mass spectrometer (GC/MS) or Fourier transform infrared (GC/FT-IR) instrument. Butyl rubber was shown to decompose under very high temperatures (400 °C or greater) by radical formation and unzipping to yield oligomers, monomers, and volatile gaseous products [11]. However, specific structures for these degradation products, identified as hydrocarbons [11], were not noted. To our knowledge, our study is the first time volatile low-molecular weight thermal-oxidative degradation products of butyl rubber and its related materials have been fully characterized.

Physical properties can relay information regarding the degradation of a material and typical change as a function of temperature and time. Consequently, our experimental accelerated aging temperatures and times were chosen such that butyl rubber degradation products were collected and detected at multiple time points correlating to a loss of up to 100% O-ring seal force, as measured by a compression stress relaxation (CSR) apparatus [6]. This physical property is of particular interest in these experiments because it is thought to directly relate to the useable lifetime of the O-ring. That is, experiments were designed to identify degradation products under conditions as close to those in which butyl rubber is typically used in the stockpile within a reasonable amount of experimental time.

Here, accelerated aging (i.e., higher aging temperatures for shorter periods of time to simulate real-life conditions) experiments were tailored to identify volatile low-molecular weight thermal-oxidative degradation species of two butyl rubber formulations provided by KCP (Butyl #6 and #10), a commercially available chlorobutyl rubber (arbitrarily named Butyl #21), Butyl #10 starting material (Laxness bromobutyl 2030), and two Butyl #10 additives (polyethylene AC-617 and Vanax MBM); a focus was placed on Butyl #10 experiments due to its superior characteristics that were measured in a previous physical properties aging study [6]. The materials were aged up to 413 total days at up to 124 °C under ambient thermal-oxidative environmental conditions (i.e., ambient room atmosphere and pressure with the addition of heat) in all but two cases. For one case, the aging atmosphere of a Butyl #10 sample was oxygen-18

($^{18}O_2$) enriched (99%). In contrast, non-oxidative thermal degradation conditions were achieved by aging Butyl #10 under an argon atmosphere.

Headspace gas over the aged samples, as outlined in the previous paragraph, was analyzed using cryofocusing gas chromatography/mass spectrometry (cryo-GC/MS). Identification of volatile degradation species for each material was accomplished by combining manual interpretation [12, 13] and a NIST library [14] match algorithm built into the data analysis software. Several degradation products were identified for each butyl rubber and its related materials with the most common being alkanes, alkenes, alcohols, ketones, and aldehydes. Comparisons between the products identified from Butyl #10 and each of its starting materials were noted. Mass spectral data obtained from unlabeled Butyl #10 was compared to those for Butyl #10 aged under isotopically enriched oxygen, which provided information regarding the origin of the characterized degradation species that contained at least one oxygen atom (i.e., the atmosphere or the polymeric macromolecule). In addition, mass spectral data obtained from aging Butyl #10 under an argon environment was compared to all samples aged under an ambient or oxygen-18 enriched atmosphere.

This work focuses on the use of mass spectrometry to identify the thermal-oxidative degradation products and selective isotopic labels of several butyl rubber formulations and one formulation’s starting materials while future work may focus on investigating the origin of individual species as they relate to the complex degradation mechanisms. Information regarding potentially dangerous chemical reactions within the system could then be identified. Ultimately, all of the information gathered could then be used to develop a sensor to detect and monitor a thermal-oxidative degradation species specific to butyl rubber under the same stockpile conditions (e.g., aging time and temperature).

2. EXPERIMENTAL

2.1. Materials

Twenty candidate butyl rubber formulations were developed by Mark Wilson at Kansas City Plant (KCP, Kansas City, MO), and the two most promising materials, arbitrarily named as Butyl #6 and Butyl #10, were sent to Sandia National Laboratories (SNL, Albuquerque, NM) [6]. A third formulation manufactured by Polyone Coporation and used previously in WR products was acquired and named Butyl #21. Table 1 depicts the complete formulations and the function of each ingredient for all three butyl samples, as provided by KCP.

O-rings of the three butyl formulations molded by RD Rubber (mold P/N 303691) fell within the allowed cross sectional diameter (103 ± 3 mils) and inner diameter (7,185 ± 14 mils) size tolerances [6]. If shrinkage variations were observed from one formulation to another, RD Rubber cut a new mold [6], which resulted in O-rings of comparable sizes. The samples were tested as received with no additional post cure or cleaning in the accelerated aging experiments.

One starting material (Lanxess bromobutyl 2030) and two additives (polyethylene AC-617 and Vanax MBM, powder form) were also provided by the manufacturer and KCP for our aging studies. It is worth noting that polyethylene AC-617 was added to the KCP formulations as an internal lubricant rather than using processing oils that could potentially cause migration and thus result in compatibility issues in WR or other applications [6]. Oxygen-18 [$^{18}O_2$, 99% enriched, purity verified in-house using residual gas analysis (RGA)] and argon gas were supplied by Sigma-Aldrich (Miamisburg, OH) and used without further purification.

Table 1. Butyl rubber candidate formulations as provided by KCP

		Butyl #		
Purpose	**Ingredient**	**6**	**10**	**21**
		PHR[a]	PHR	PHR
Polymer	Exxon Exxpro 3433	100		
Polymer	Exxon chlorobutyl HT1066			100
Polymer	Lanxess bromobutyl 2030		100	
Antioxidant	CYANOX 2246			1.5
Reinforcing filler	N550 carbon black	65	65	33
Reinforcing filler	N330 carbon black			33
Processing aid (internal lubricant)	Polyethylene AC-617	5	5	
Accelerator	Advance 5364 ZDMC Pellets-80			1.88
Activator	Stearic acid	0.5		
Activator/Vulcanizer	Zinc oxide (French process)	2	5	5
Cure co-agent	HVA-2 or Vanax MBM		5	
Activator/Vulcanizer	SP 1045 resin	5		

[a] PHR = parts per hundred rubber

2.2. Accelerated Aging

Aging temperature (109 and 124 °C) and times (up to 413 total days) were selected using compression stress relaxation (CSR) data for various aging conditions in a previous butyl rubber study [6]. The CSR apparatus consists of a compression frame or “jig” made up of two parallel metal plates and an electronic force testing machine. The restoring force, *F*, caused by the strained material between the jig plates is measured. In these experiments, O-rings with all three formulations were cut into pieces (typically 4 to 5) and laid out on the CSR jig plate with reasonable spacing between the samples. This sampling technique not only increased the allowable air flow between samples as they were strained but also minimized possible diffusion limited oxidation effects from use of an intact O-ring or pieces of O-ring touching each other while strained. The measured force from the CSR apparatus directly relates to the degradation parameter known as O-ring sealing force, which could be the most important parameter for determining the health of an O-ring seal or estimating its lifetime. The sealing force measurements were acquired isothermally for O-rings aged at temperatures at and between 64 and 124 °C and times up to several hundred total days. Plots of generating force *vs.* aging time for a specific temperature could thus be created [6]. Consequently, the aging temperature and corresponding aging time(s) for these experiments were chosen such that reasonable levels of physical property degradation (i.e., loss of O-ring sealing force) were seen in an acceptable amount of time for all three butyl formulations.

Previous results indicated that each butyl formulation had differing amounts of sealing force remaining at a given temperature for the same aging time point. For example, the remaining percentage of sealing force for 60 total days of aging at 109 °C for Butyl #6, #10, and #21 was ~20%, ~70%, and ~10%, in that order [6]. Due to Butyl #10’s remarkable retention of sealing strength as compared to the other two formulations under the same conditions, the sample was aged for an extended period of time and at a higher temperature. Specifically, the Butyl #10 sample was aged for 216 total days at 109 °C (~50% sealing force remaining [6]) then at 124 °C for 166 total days before a final aging time of 31 total days at 109 °C (i.e., 247 total days at 109 °C and 166 total days at 124 °C for a total of 413 total days of aging). In the end, it was determined that this Butyl #10 sample set had ~20% of sealing force remaining [6], which was numerically close to what was determined to be the acceptable useable lifetime of the O-ring.

Due to time and budget restraints, the Butyl #10 starting material and additives were aged up to 61 and 63 total days, respectively (Table 2). Ideally, the aging conditions would have matched that of Butyl #10 for all species and thus allowed for direct comparisons at each time point. For these studies, aging up to ~60 total days sufficiently describes the material as it is not actually in the stockpile in its pure form, and formulations #6 and #21 proved to have a much shorter lifetime than #10 [6]. In addition, Butyl #10 is a formulation widely used in the stockpile and thus characterizing its degradation is of high importance.

Samples (Butyl #6, #10, and #21; Laxness bromobutyl 2030; polyethylene AC-617; and Vanax MBM) were sealed inside separate stainless steel vessels (5-10 cc) with gold plated copper gaskets that provided a barrier between the aged sample and the gaseous environment surrounding the vessel. The gold plating on the gaskets also minimized possible contamination of the headspace from oxidation products that could form at elevated temperatures from materials that are known to outgas (e.g., organic O-rings) and removed any potential copper catalyzed degradation mechanisms. Experiments for all accelerated aging conditions were conducted in duplicate within an air circulation oven. For a single sample, data was collected in series at successive time points (e.g., first, second, third, *etc*.) where the total amount of time the sample was aged is reported. In other words, the headspace gas was allowed to regenerate between collection times.

Material masses were chosen such that sufficient signal from the volatile products was present for detection across the span of aging times without maxing out the instrument detector. Most samples were filled under ambient pressure room air [~620 Torr (~83 kPa) at 25 °C in Albuquerque, NM)] before aging. Butyl #10 was also aged under a backfill pressure [~130 Torr (~17.3 kPa) at 25 °C post vessel evacuation at ~1 x 10^{-6} Torr (~1.3 x 10^{-7} kPa)] of $^{18}O_2$ in an effort to determine if oxygen originated from the gaseous environment or macromolecular structure of the polymer for the applicable degradation products. The $^{18}O_2$ backfill pressure was chosen so that the partial pressure of oxygen in the experimental vessel at the elevated aging temperature was slightly greater than that of ambient air in our laboratory (i.e., atmospheric conditions). This pressure ensured enough oxygen was present for degradation to occur under simulated ambient conditions [6]. Similarly, Butyl #10 was also aged under a backfill pressure of argon (i.e., non-oxidative thermal degradation conditions) so that a comparison to thermal-oxidative data obtained was available. A summary of the materials and the conditions under which they were aged is presented in Table 2.

Table 2. Summary of aged butyl rubber materials and their conditions

Material	Amounts Aged (mg)	Aging Gas	Aging Temperature (°C)	Aging Times (total days)
Butyl #6	153 & 119	Air	109	30 & 61
Butyl #10[a]	116 & 113	Air	109 & 124	30, 60, 106, & 216, & 413
	123 & 125	$^{18}O_2$	109	30 & 61
	130 & 146	Argon	109	30 & 92
Butyl #21	130 & 156	Air	109	30 & 61
Laxness bromobutyl 2030	175 & 108	Air	109	30 & 61
Polyethylene AC-617	42 & 39	Air	109	31 & 63
Vanax MBM	50 & 38	Air	109	31 & 63

[a] Butyl #10 was aged at 109 °C for up to 216 total days then at 124 °C for 166 total days before a final aging time of 31 total days at 109 °C (i.e., 247 total days at 109 °C and 166 total days at 124 °C for a total of 413 total days of aging), as described in the text.

2.3. Instrumentation

Cryofocusing gas chromatography coupled with a mass spectrometer (cryo-GC/MS) was used to preconcentrate, separate, detect, and identify the volatile compounds that evolved from the aged samples. Headspace (10 cc) over the samples was extracted into the 3-stage preconcentrator (Model 7100A, Entech Instruments, Inc., Simi Valley, CA). The gas packet was first trapped

(-150 °C) onto and then desorbed from (100 °C) a glass bead trap before transmission to a Tenax trap (trapped -100 °C, desorbed 180 °C). Following the final preconcentration stage of on-column focusing (-160 °C), the gas was transported to the GC through a transfer line (100 °C).

The preconcentrated gas was rapidly injected into the back inlet (240 ºC) of a GC (Model 6890N, Agilent Technologies, Santa Clara, CA) equipped with a DB-5MS column (0.25 mm x 60 m, Agilent). GC settings were optimized to separate the compounds of interest effectively over the course of 52 min: the GC oven was held at an initial temperature of -40 °C for 2 min, then ramped to 30 °C (9 °C min-1), ramped to 150 °C (3 °C min-1), and finally held at 150 °C for 2 min. Argon blanks were run between samples to eliminate potential degradation species carryover.

Mass spectral analysis was performed in conjunction with the GC separation using a GCMate II mass spectrometer (Jeol USA, Peabody, MA) fitted with an electron ionization (EI) source operated in positive mode at 70 eV. The ions were scanned from 12 to 220 Da in 0.49 s with a maximum resolution of 1,000 ($m/\Delta m$). Perfluorokerosene (PFK) was used as an instrument calibrant over the entire mass range scanned. Data was analyzed using TSSPro 3.0 (v. 300.0440, Shrader Analytical and Consulting Laboratories, Inc., Detroit, MI), and mass spectra were compared to those in the NIST Mass Spectral Library [14].

3. RESULTS AND DISCUSSION

Three butyl rubber formulations (Butyl #6 and #10 from KCP and commercially available Butyl #21) along with Butyl #10 starting material (Laxness bromobutyl 2030) and additives (polyethylene AC-617 and Vanax MBM) were aged under accelerated thermal-oxidative conditions for all but one experiment where Butyl #10 was aged under argon (i.e., non-oxidative thermal degradation conditions) for comparison purposes. Post aging, the volatile low-molecular weight degradation species in the headspace above the samples were preconcentrated by cryofocusing, separated using a gas chromatogram, and analyzed with a mass spectrometer (cryo-GC/MS). Under identical sampling conditions, GC retention times as well as mass spectral peaks produced by an electron ionization (EI) source are highly reproducible [12, 15] for a given species, which enables the experimentalist to identify unknown species using information gathered from a set of known compounds and/or a library database (e.g., homemade or NIST). Moreover, monitoring of mass spectral shifts related to isotopic enrichment of the sample or its aging atmosphere can lead to discoveries regarding the origin of the degradation species and then related back to the complex macromolecular structure of the polymer.

3.1. Data Analysis and Interpretation

Cryo-GC/MS data for all compounds was collected in duplicate and showed similar results for a given set of experimental conditions, as described in the sections that follow. Species have been identified and numbered according to increasing retention time as well as visually depicted in tabular form. Throughout the text in a given section, each degradation product will be referred to by its “compound name” followed by its corresponding “**{#}**”. Peaks observed in the chromatograms that are not labeled represent common GC column bleed contaminants or degradation species that were not present in quantities sufficiently above the background noise for a distinct chemical assignment.

GC peak intensities assigned to a given species generally grew in intensity with increasing aging time, while some products were not present in a detectable amount until the material had been aged for longer aging times. However, it should be noted that these studies were not quantitative. Thus, relative peak areas for the detected products were not calculated or reported here. However, the relative intensities within a single run are similar when sister samples are compared. GC retention times and the identified degradation species for a given sample aged for varying amounts of time were strikingly similar, as illustrated in the figures that follow. Repeatability in our data for gas chromatograms and the representative mass spectrum for a GC peak at a certain retention time adds assurance to our experimental design and results as well as instrument performance.

Structural assignments for each degradation product were made by manual interpretation [12, 13] and a NIST library [14] comparison of the mass spectral data. The correlation factor or specificity of the library match, reported as a percentage, was strongly considered when chemical assignments were made. A digital subtraction of the background spectrum on either side of the GC peak of interest was necessary. This methodology introduced minimal error for cases in which analyte intensities were low or coelution with a neighboring species and/or an impurity ensued. The correlation factors for the compounds reported here were most commonly ≥ 80%

(i.e., the specificity of the library match). However, it should be noted that library mass spectra fragmentation patterns are created using pure compounds rather than complex mixtures, which is potentially problematic for the identification of unknowns in a complex matrix such as the ones described here. In fact, it was difficult to distinguish the exact structural isomer of some degradation products, specifically for some hydrocarbons. In these cases, we report the best match for the structure based on all butyl rubber compounds analyzed (i.e., comparing retention times and mass spectra across multiple data sets taken over the course of several years). The instances in which we were uncertain about the chemical structure assignments are noted in the text and tables by italicizing the corresponding degradation product compound names. For example, we assigned compound ***{4}*** in Table 3 as *3-methyl-1-butene* based on commonalities amongst all mass spectra for all aged species, but it was difficult to establish exact values for the experimental relative intensities of the *m/z* ratios *vs.* the expected intensities in the NIST library [14] for other methyl-butene compounds (ex., 2-methyl-2-butene). Thus, the assignment was made and a note that this may be another “methyl-butene variation” was added to the table.

3.2. Butyl #6

Seventeen volatile compounds were identified in the headspace of duplicate samples of Butyl #6 aged under ambient air for 30 and 61 total days in series at 109 °C (Figure 2 and Table 3). Nine of the compounds were identified as hydrocarbons – alkanes and alkenes: 2-methyl-1-propene **{1}**, *3-methyl-1-butene* ***{4}***, *methyl-2-butene* ***{6}***, C_6H_{12} ***{8}***, 2,2,4-trimethyl-pentane **{11}**, 2,4,4-trimethyl-1-pentene **{12}**, *2,4,4-trimethyl-2-pentene* ***{14}***, 2,3-dimethyl-1-hexene **{15}**, and *3,4,4-trimethyl-2-pentene* ***{16}***. Detected oxygenated species included an alcohol (methyl alcohol **{3}**), four ketones (acetone **{5}**, 3-methyl-2-butanone **{10}**, 3,3-dimethyl-2-butanone **{13}**, and 4,4-dimethyl-2-pentanone **{17}**), an aldehyde (2,2-dimethyl propanal **{9}**), and an acetate (methyl acetate **{7}**). Since Butyl #6 is a brominated butyl rubber, it was not surprising that bromomethane **{2}** was also detected.

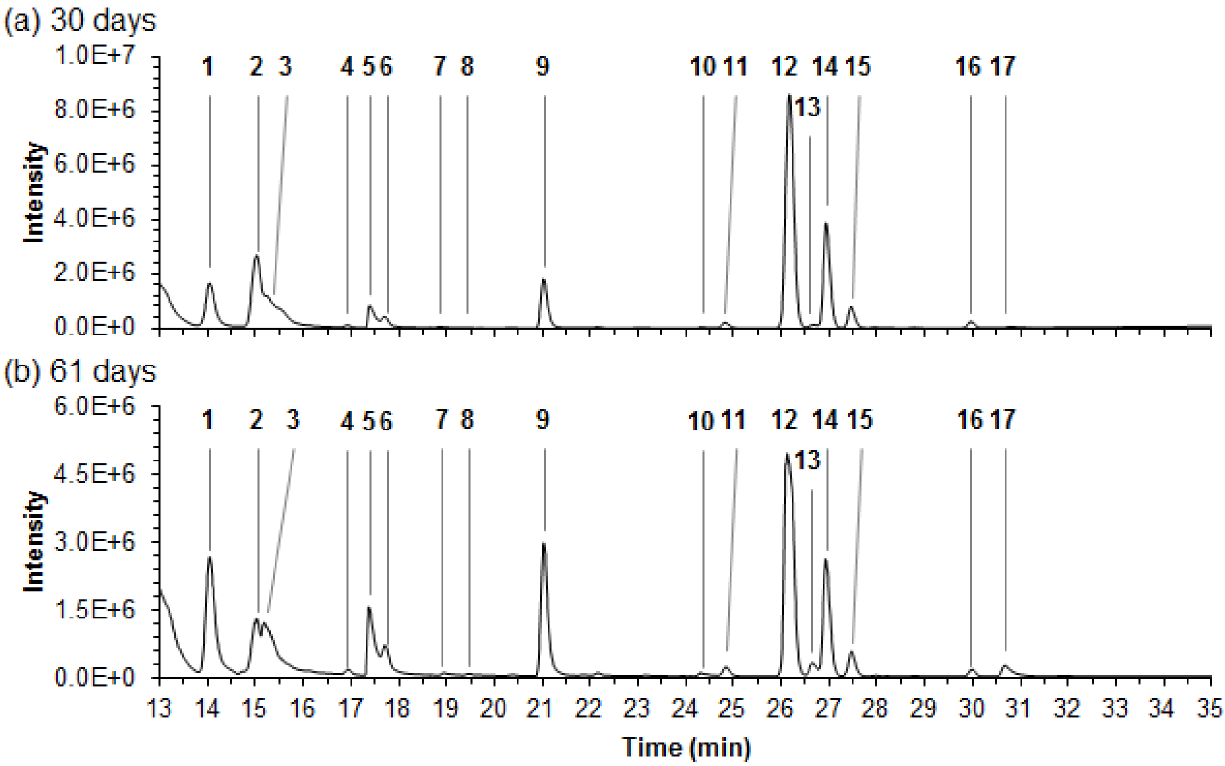
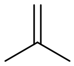


Figure 2. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Butyl #6 aged under an ambient atmosphere at 109 °C for (a) 30 and (b) 61 total days in series. The numbers 1-17 across the top of the chromatograms correspond to the identified degradation products as listed in Table 3.

Table 3. Low-molecular weight volatile Butyl #6 thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 61 total days in series at 109 °C[a]



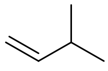
2-methyl-1-propene **{1}**
(C_4H_8, 56.0626)

CH_3Br

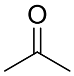
bromomethane **{2}**
(CH_3Br, 93.9418)

—OH

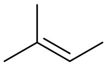
methyl alcohol **{3}**
(CH_4O, 32.0262)



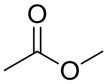
3-methyl-1-butene ***{4}***
(C_5H_{10}, 70.0783)[b]



acetone **{5}**
(C_3H_6O, 58.0419)



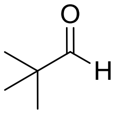
2-methyl-2-butene ***{6}***
(C_5H_{10}, 70.0783)[c]



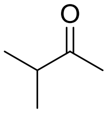
methyl acetate **{7}**
($C_3H_6O_2$, 74.0368)

C_6H_{12}

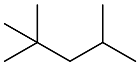
C_6H_{12} ***{8}***
(C_6H_{12}, 84.0939)[d]



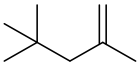
2,2-dimethyl propanal **{9}**
($C_5H_{10}O$, 86.0732)



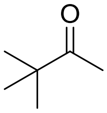
3-methyl-2-butanone **{10}**
($C_5H_{10}O$, 86.0732)



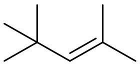
2,2,4-trimethyl-pentane **{11}**
(C_8H_{18}, 114.1409)



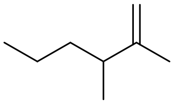
2,4,4-trimethyl-1-pentene **{12}**
(C_8H_{16}, 112.1252)



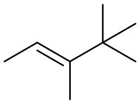
3,3-dimethyl-2-butanone **{13}**
($C_6H_{12}O$, 100.0888)



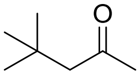
2,4,4-trimethyl-2-pentene ***{14}***
(C_8H_{16}, 112.1252)[e]



2,3-dimethyl-1-hexene **{15}**
(C_8H_{16}, 112.1252)



3,4,4-trimethyl-2-pentene ***{16}***
(C_8H_{16}, 112.1252)[f]



4,4-dimethyl-2-pentanone **{17}**
($C_7H_{14}O$, 114.1045)

[a] Compounds are numbered by increasing retention time (see Figure 2). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* methyl-butene variation

[c] *Structural assignment:* methyl-butene variation

[d] *Structural assignment:* C_6H_{12} variation, structural assignment uncertain

[e] *Structural assignment:* trimethyl-pentene variation

[f] *Structural assignment:* trimethyl-pentene variation, might be 2,3,4-trimethyl-2-pentene

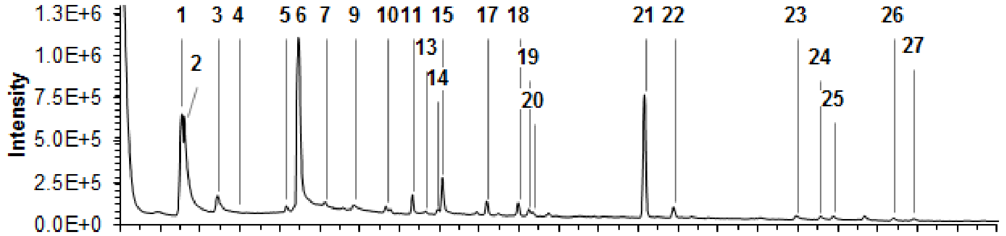
3.3. Butyl #10

Twenty-seven volatile compounds were present in the headspace above duplicate samples of Butyl #10 aged under ambient air for 30, 60, 106, and 216 totals days in series at 109 °C (Figure 3a-d and Table 4). In order to relate the compound's extraordinary physical properties [6], as compared to the other butyl rubber formulations (Table 1), to the degradation species detected, the samples were aged for an additional 197 total days in series. The conditions were as follows: samples aged for 216 total days were then aged at 124 °C for 166 total days followed by 31 total days at 109 °C (i.e., 247 total days at 109 °C and 166 total days at 124 °C for a total of 413 total days of aging).

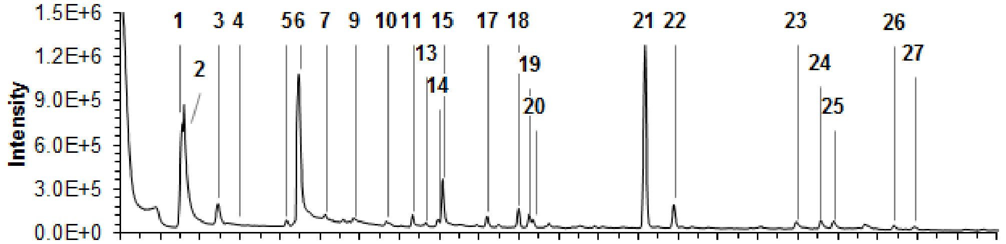
Nearly half of the twenty-seven identified Butyl #10 degradation products were hydrocarbons where two were alkanes (3-methyl pentane **{11}** and methyl cyclopentane **{17}**) and eleven were alkenes (2-methyl-1-propene **{1}**, 1-pentene **{5}**, *2-pentene {7}*, 1-hexene **{13}**, 2,4-dimethyl-1-pentene **{18}**, 2,4-dimethyl-2-pentene **{19}**, 2,4-dimethyl 1,4-pentadiene **{20}**, 2,4,4-trimethyl-1-pentene **{21}**, *2,4,4-trimethyl-2-pentene {22}*, *3,5,5-trimethyl-2-hexene {26}*, and 2,4,4-trimethyl-1-hexene **{27}**). The large majority of the remaining degradation species were oxygenated and belonged to the following chemical families: alcohols (methyl alcohol **{4}** and tert-butyl alcohol **{9}**), ketones (acetone **{6}**, 2-butanone **{16}**, 4,4-dimethyl-2-pentanone **{23}**, and 2,4-dimethyl-3-pentanone **{24}**), aldehydes (acetaldehyde **{2}**, 2-methyl propanal **{10}**, methylacrolein **{12}**, butanal **{14}**, and 2,2-dimethyl propanal **{15}**), and furans (tetrahydro-2,2,4,4-tetramethyl-furan **{25}**). Since Butyl #10 contains brominated starting material (Lanxess bromobutyl 2030), it was not surprising that bromomethane **{3}** was also detected. Finally, carbon disulfide **{8}** was detected with about a 95% library match factor [14] only after the samples were aged for 413 total days in series. Since this product took many days to form and had low signal intensity compared to the other degradation species, a very small concentration of sulfur may have been present as an impurity in one of the Butyl #10 starting materials.

A straightforward comparison of the results of this extended aging study (Figure 3e) to those for samples aged up to 216 total days in series (Figure 3a-d) shows that most of the same products are seen in all spectra. Also, the overall signal of the degradation species is greatly diminished as the sample is aged for long periods of time. [Note, the slight shift in GC retention times for data collected after 216 total days of aging is due to a minor change in the instrument setup, likely a trimming of the GC column, during the time between data collection points.] As sample aging progresses in time, the physical properties of the sample are most often diminished, as is the case for butyl rubber [6]. For example, the source for 3-methyl pentane **{11}** is likely completely gone after 106 total days of aging (Figure 3). In addition, the drastic drop of overall signal intensity means there are fairly small amounts of three species (carbon disulfide **{8}**, methylacrolein **{12}**, and 2-butanone **{16}**) present at 413 total days of aging. Aside from the likely sulfur impurity, the latter two degradation products were also not detectable at 216 or fewer total days of aging, which may be due to the availability of different mechanisms as the polymer degrades.

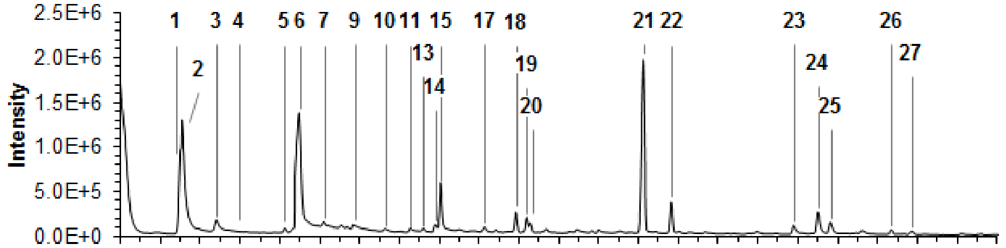
(a) 30 days



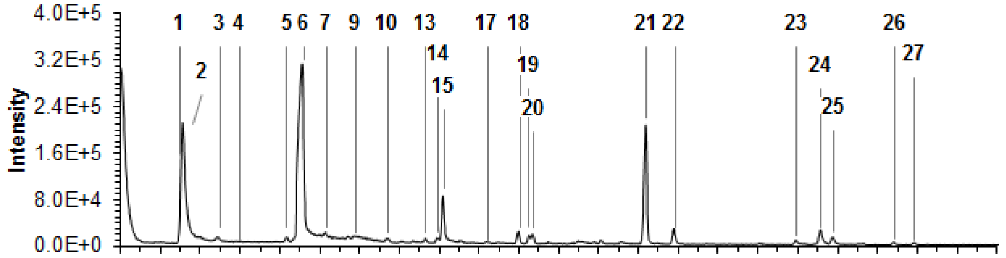
(b) 60 days



(c) 106 days



(d) 216 days



(e) 413 days

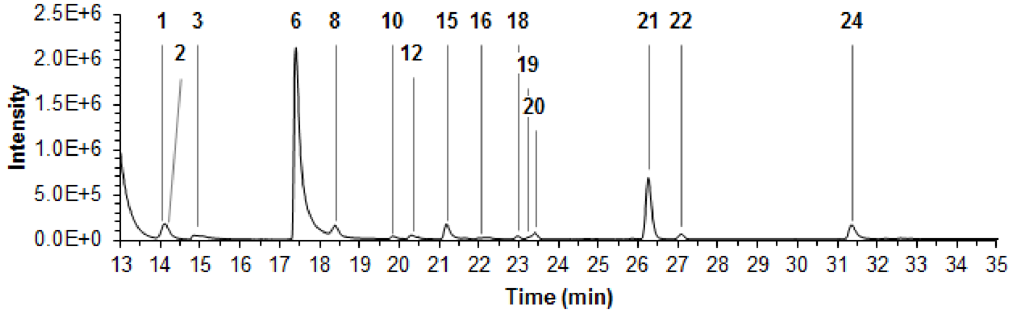
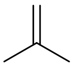
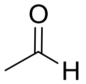


Figure 3. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Butyl #10 aged under an ambient atmosphere at 109 °C for (a) 30, (b) 60, (c) 106, and (d) 216 total days in series. As described in the text, sample (e) was aged for a total of 413 days in series using a combination of temperature and time points. The numbers 1-27 across the top of the chromatograms correspond to the identified degradation products as listed in Table 4.

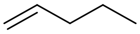
Table 4. Low-molecular weight volatile Butyl #10 thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 216 total days at 109 °C and a combination of temperatures for up to 413 total days in series[a]

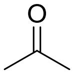

2-methyl-1-propene **{1}**
(C_4H_8, 56.0626)

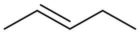

acetaldehyde **{2}**
(C_2H_4O, 44.0262)

CH_3Br
bromomethane **{3}**
(CH_3Br, 93.9418)

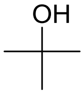
—OH
methyl alcohol **{4}**
(CH_4O, 32.0262)

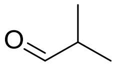

1-pentene **{5}**
(C_5H_{10}, 70.0783)

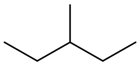

acetone **{6}**
(C_3H_6O, 58.0419)

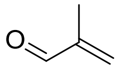

2-pentene {7}
(C_5H_{10}, 70.0783)[b]

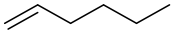
S=C=S
carbon disulfide **{8}**
(CS_2, 75.9441)

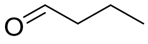

tert-butyl alcohol **{9}**
($C_4H_{10}O$, 74.0732)

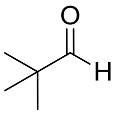

2-methyl propanal **{10}**
(C_4H_8O, 72.0575)

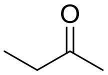

3-methyl pentane **{11}**
(C_6H_{14}, 86.1096)

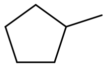

methylacrolein **{12}**
(C_4H_6O, 70.0419)

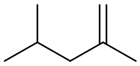

1-hexene **{13}**
(C_6H_{12}, 84.0939)

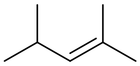

butanal **{14}**
(C_4H_8O, 72.0575)

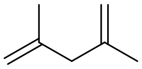

2,2-dimethyl propanal **{15}**
($C_5H_{10}O$, 86.0732)

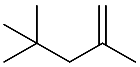

2-butanone **{16}**
(C_4H_8O, 72.0575)

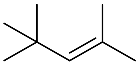

methyl cyclopentane **{17}**
(C_6H_{12}, 84.0939)

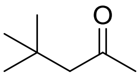

2,4-dimethyl-1-pentene **{18}**
(C_7H_{14}, 98.1096)

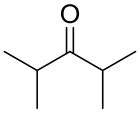

2,4-dimethyl-2-pentene **{19}**
(C_7H_{14}, 98.1096)

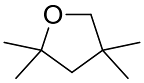

2,4-dimethyl 1,4-pentadiene **{20}**
(C_7H_{12}, 96.0939)

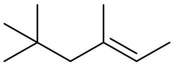

2,4,4-trimethyl-1-pentene **{21}**
(C_8H_{16}, 112.1252)

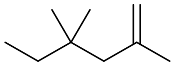

2,4,4-trimethyl-2-pentene {22}
(C_8H_{16}, 112.1252)[c]


4,4-dimethyl-2-pentanone **{23}**
($C_7H_{14}O$, 114.1045)


2,4-dimethyl-3-pentanone **{24}**
($C_7H_{14}O$, 114.1045)


tetrahydro-2,2,4,4-tetramethyl-furan **{25}**
($C_8H_{16}O$, 128.1201)


3,5,5-trimethyl-2-hexene {26}
(C_9H_{18}, 126.1409)[d]


2,4,4-trimethyl-1-hexene **{27}**
(C_9H_{18}, 126.1409)

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[a] Compounds are numbered by increasing retention time (see Figure 3). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* C_5H_{10} variation

[c] *Structural assignment:* trimethyl-pentene variation

[d] *Structural assignment:* trimethyl-hexene variation, might be 2,5,5-trimethyl-2-hexene

3.3.1. Starting Material: Lanxess bromobutyl 2030

Twenty-three volatile compounds were present in the headspace of duplicate samples of Lanxess bromobutyl 2030 Butyl #10 starting material aged under ambient air for 30 and 61 totals days in series at 109 °C (Figure 4 and Table 5). Seven alkanes (2-methyl pentane **{6}**, 3-methyl pentane

{7}, hexane **{8}**, *2,2-dimethyl-pentane {11}*, methyl cyclopentane **{12},** cyclohexane **{15}**, and 2,2,4-trimethyl-pentane **{16}**) and four alkenes (2-methyl-1-propene **{1}**, 2,4-dimethyl-1-pentene **{13}**, 2,4-dimethyl-2-pentene **{14}**, and 2,4,4-trimethyl-1-pentene **{18}**) composed the collection of eleven hydrocarbon species that were detected. Most of the nine oxygenated degradation products were ketones (acetone **{4}**, 2-butanone **{10}**, 2-pentanone **{17}**, 3,3-dimethyl-2-butanone **{19}**, 4,4-dimethyl-2-pentanone **{21}**, and 2,4-dimethyl-3-pentanone **{22}**) while the others were aldehydes (acetaldehyde **{2}** and 2,2-dimethyl propanal **{9}**) and a dioxane (1,4-dioxane **{20}**). Since Lanxess bromobutyl 2030 is a brominated material, it was not surprising that bromomethane **{3}**, bromoethane **{5}**, and *1-bromo-pentane {23}* were also detected.

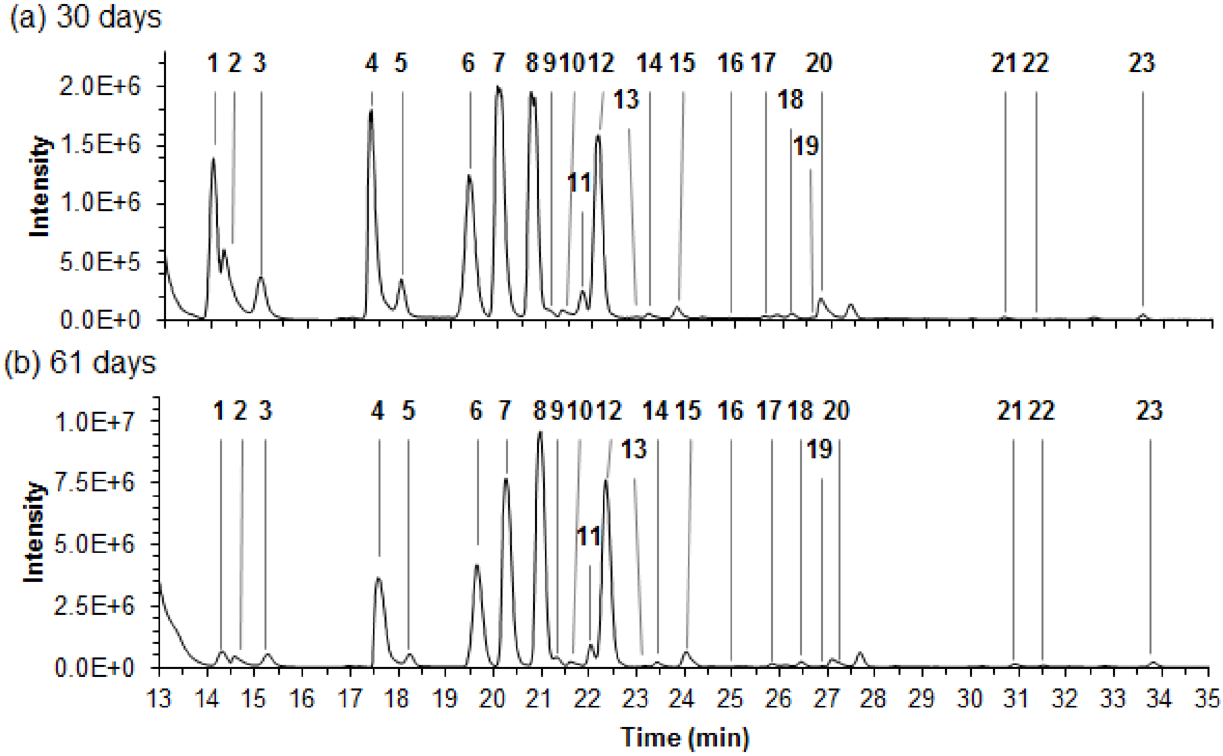
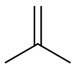
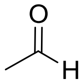
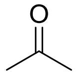
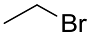
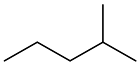
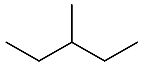
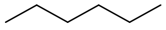
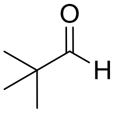
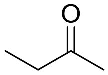
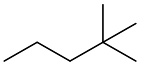
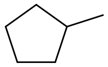
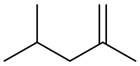
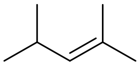
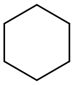
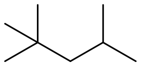
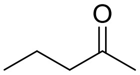
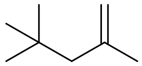
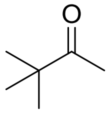
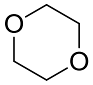
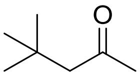
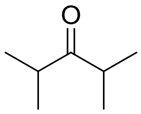
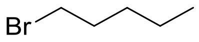


Figure 4. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Lanxess bromobutyl 2030 aged under an ambient atmosphere at 109 °C for (a) 30 and (b) 61 total days in series. The numbers 1-23 across the top of the chromatograms correspond to the identified degradation products as listed in Table 5.

Table 5. Low-molecular weight volatile Lanxess bromobutyl 2030 thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 61 total days in series at 109 °C[a]

 2-methyl-1-propene **{1}** (C_4H_8, 56.0626)	 acetaldehyde **{2}** (C_2H_4O, 44.0262)	CH_3Br bromomethane **{3}** (CH_3Br, 93.9418)	 acetone **{4}** (C_3H_6O, 58.0419)
 bromoethane **{5}** (C_2H_5Br, 107.9575)	 2-methyl pentane **{6}** (C_6H_{14}, 86.1096)	 3-methyl pentane **{7}** (C_6H_{14}, 86.1096)	 hexane **{8}** (C_6H_{14}, 86.1096)
 2,2-dimethyl propanal **{9}** ($C_5H_{10}O$, 86.0732)	 2-butanone **{10}** (C_4H_8O, 72.0575)	 *2,2-dimethyl-pentane* ***{11}*** *(C_7H_{16}, 100.1252)*[b]	 methyl cyclopentane **{12}** (C_6H_{12}, 84.0939)
 2,4-dimethyl-1-pentene **{13}** (C_7H_{14}, 98.1096)	 2,4-dimethyl-2-pentene **{14}** (C_7H_{14}, 98.1096)	 cyclohexane **{15}** (C_6H_{12}, 84.0939)	 2,2,4-trimethyl-pentane **{16}** (C_8H_{18}, 114.1409)
 2-pentanone **{17}** ($C_5H_{10}O$, 86.0732)	 2,4,4-trimethyl-1-pentene **{18}** (C_8H_{16}, 112.1252)	 3,3-dimethyl-2-butanone **{19}** ($C_6H_{12}O$, 100.0888)	 1,4-dioxane **{20}** ($C_4H_8O_2$, 88.0524)[c]
 4,4-dimethyl-2-pentanone **{21}** ($C_7H_{14}O$, 114.1045)	 2,4-dimethyl-3-pentanone **{22}** ($C_7H_{14}O$, 114.1045)	 *1-bromo-pentane* ***{23}*** *($C_5H_{11}Br$, 150.0044)*[d]	

[a] Compounds are numbered by increasing retention time (see Figure 4). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* C_7H_{16} variation

[c] *Structural assignment:* structural assignment uncertain

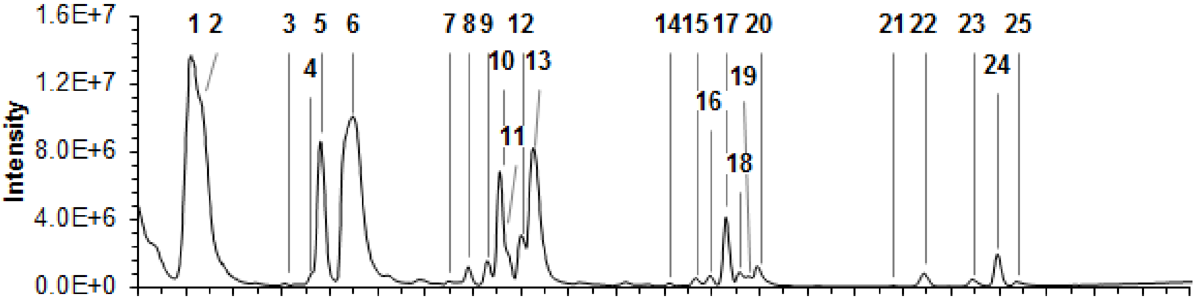
[d] *Structural assignment:* bromo-pentane variation, might be 2-bromo-pentane

3.3.2. Additive: Polyethylene AC-617

Twenty-five volatile compounds were present in the headspace of duplicate samples of polyethylene AC-617 Butyl #10 internal lubricant additive aged under ambient air for 31 and 63 totals days in series at 109 °C (Figure 5 and Table 6). The sixteen identified hydrocarbons – alkanes and alkenes – included: butane **{1}**, 1-pentene **{4}**, pentane **{5}**, 3-methyl pentane **{8}**, 1-hexene **{9}**, hexane **{10}**, *methyl-pentene* ***{11}***, 3-methyl hexane **{14}**, 3-ethyl pentane **{15}**, *1-heptene* ***{16}***, heptane **{17}**, *C_7H_{14}* ***{19}***, *3-methyl-4-methylene-hexane* ***{21}***, 3-methyl heptane

{22}, 3-methylene heptane **{23}**, and octane **{24}**. The nine remaining volatile species detected included alcohols, ketones, and aldehydes: acetaldehyde **{2}**, methyl alcohol **{3}**, acetone **{6}**, tert-butyl alcohol **{7}**, butanal **{12}**, 2-butanone **{13}**, 2-pentanone **{18}**, 3-pentanone **{20}**, and 2-hexanone **{25}**.

(a) 31 days



(b) 63 days

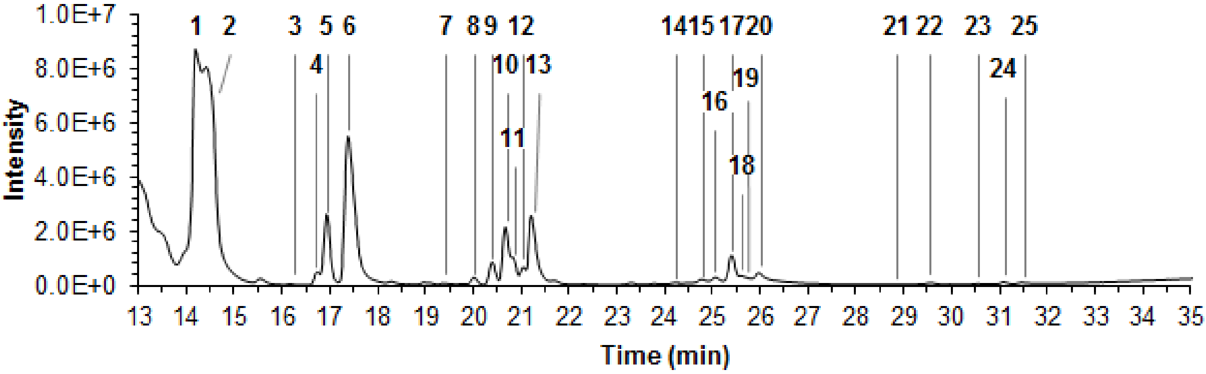
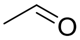
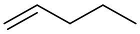
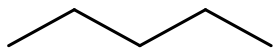
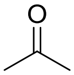
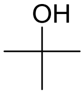
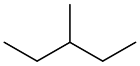
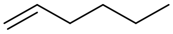
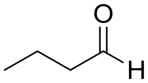
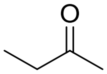
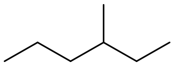
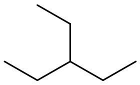
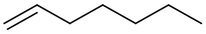
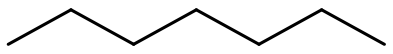
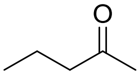
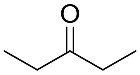
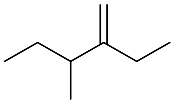
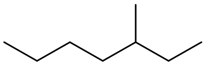
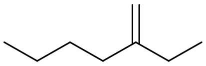
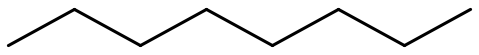
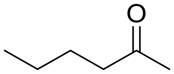


Figure 5. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over polyethylene AC-617 aged under an ambient atmosphere at 109 °C for (a) 31 and (b) 63 total days in series. The numbers 1-25 across the top of the chromatograms correspond to the identified degradation products as listed in Table 6.

Table 6. Low-molecular weight volatile polyethylene AC-617 thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 63 total days in series at 109 °C[a]

 butane **{1}** (C_4H_{10}, 58.0783)	 acetaldehyde **{2}** (C_2H_4O, 44.0262)	—OH methyl alcohol **{3}** (CH_4O, 32.0262)	 1-pentene **{4}** (C_5H_{10}, 70.0783)	
 pentane **{5}** (C_5H_{12}, 72.0939)	 acetone **{6}** (C_3H_6O, 58.0419)	 tert-butyl alcohol **{7}** ($C_4H_{10}O$, 74.0732)	 3-methyl pentane **{8}** (C_6H_{14}, 86.1096)	
 1-hexene **{9}** (C_6H_{12}, 84.0939)	 hexane **{10}** (C_6H_{14}, 86.1096)	C_6H_{12} *methyl-pentene* ***{11}*** *(C_6H_{12}, 84.0939)*[b]	 butanal **{12}** (C_4H_8O, 72.0575)	
 2-butanone **{13}** (C_4H_8O, 72.0575)	 3-methyl hexane **{14}** (C_7H_{16}, 100.1252)	 3-ethyl pentane **{15}** (C_7H_{12}, 96.0939)	 *1-heptene* ***{16}*** *(C_7H_{14}, 98.1096)*[c]	
 heptane **{17}** (C_7H_{16}, 100.1252)	 2-pentanone **{18}** ($C_5H_{10}O$, 86.0732)	C_7H_{14} *C_7H_{14}* ***{19}*** *(C_7H_{14}, 98.1096)*[d]	 3-pentanone **{20}** ($C_5H_{10}O$, 86.0732)	 *3-methyl-4-methylene-hexane* ***{21}*** *(C_8H_{16}, 112.1252)*[e]
 3-methyl heptane **{22}** (C_8H_{18}, 114.1409)	 3-methylene heptane **{23}** (C_8H_{16}, 112.1252)	 octane **{24}** (C_8H_{18}, 114.1409)	 2-hexanone **{25}** ($C_6H_{12}O$, 100.0888)	

[a] Compounds are numbered by increasing retention time (see Figure 5). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* C_6H_{12} variation

[c] *Structural assignment:* C_7H_{14} variation

[d] *Structural assignment:* C_7H_{14} variation

[e] *Structural assignment:* C_8H_{16} variation

3.3.3. Additive: Vanax MBM

Nine volatile compounds were present in the headspace of duplicate samples of Vanax MBM Butyl #10 curing co-agent aged under ambient air for 31 and 63 totals days in series at 109 °C (Figure 6 and Table 7). Three alkenes (2-methyl-1-propene **{1}**, 1-pentene **{3}**, and *2-methyl-2-butene {4}*), an alcohol (tert-butyl alcohol **{6}**), three ketones (acetone **{5}**, 2-butanone **{8}**, and 2-pentanone **{9}**), and two aldehydes (acetaldehyde **{2}** and butanal **{7}**) comprised the complete list of degradation products detected for this additive material.

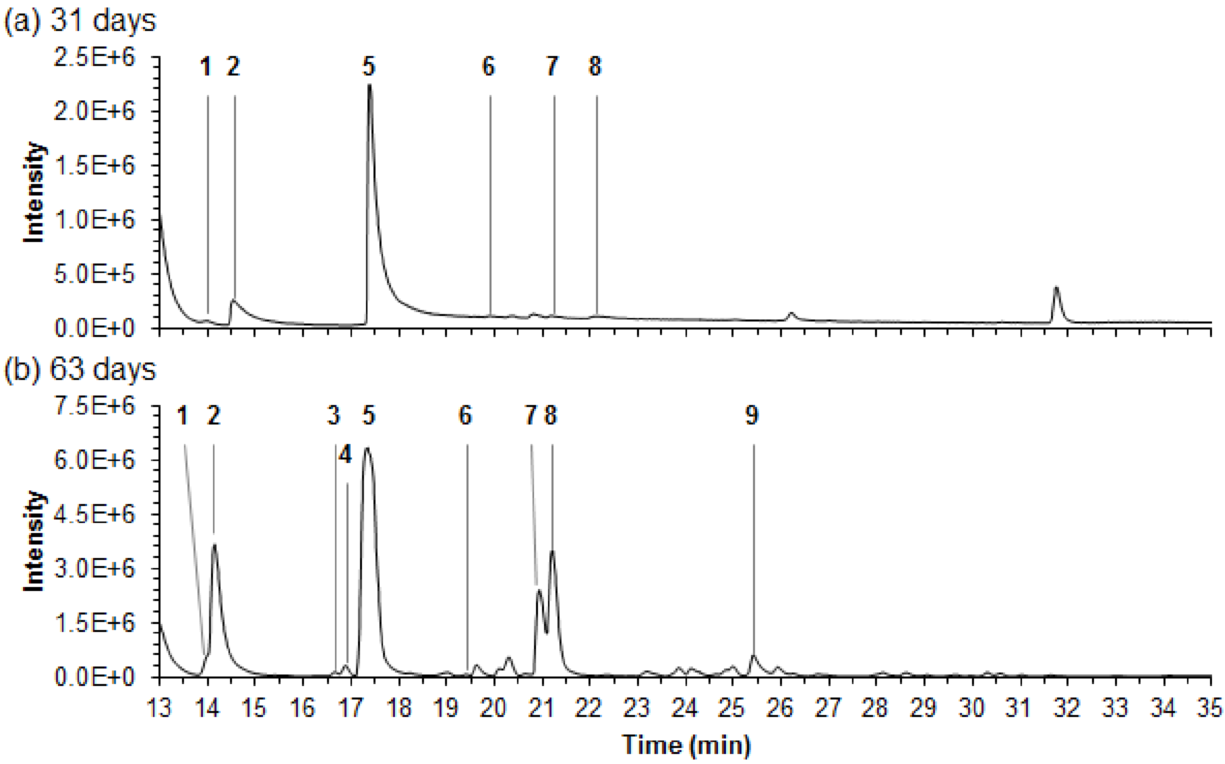
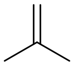
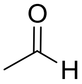
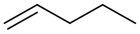
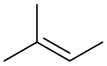
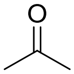
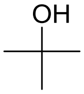
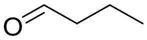
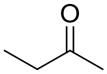
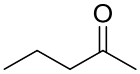


Figure 6. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Vanax MBM aged under an ambient atmosphere at 109 °C for (a) 31 and (b) 63 total days in series. The numbers 1-9 across the top of the chromatograms correspond to the identified degradation products as listed in Table 7.

Table 7. Low-molecular weight volatile Vanax MBM thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 63 total days in series at 109 °C[a]

 2-methyl-1-propene **{1}** (C_4H_8, 56.0626)	 acetaldehyde **{2}** (C_2H_4O, 44.0262)	 1-pentene **{3}** (C_5H_{10}, 70.0783)	 *2-methyl-2-butene* ***{4}*** *(C_5H_{10}, 70.0783)*[b]	 acetone **{5}** (C_3H_6O, 58.0419)
 tert-butyl alcohol **{6}** ($C_4H_{10}O$, 74.0732)	 butanal **{7}** (C_4H_8O, 72.0575)	 2-butanone **{8}** (C_4H_8O, 72.0575)	 2-pentanone **{9}** ($C_5H_{10}O$, 86.0732)	

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[a] Compounds are numbered by increasing retention time (see Figure 6). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* C_5H_{10} variation

3.3.4. Oxygen-18 Enriched Atmosphere

Two samples of Butyl #10 were aged under enriched oxygen ($^{18}O_2$) for 30 and 61 total days in series at 109 °C (Figure 7). A comparison of the GC chromatograms from these experiments to those obtained for Butyl #10 aged under laboratory air showed the applicable degradation products had virtually the same retention times despite the presence of isotopic labels (Figure 3 and Table 4). Thus, we can conclude that isotopic labels did not change the underlying degradation mechanisms of Butyl #10. Representative mass spectra for a certain GC time region for Butyl #10 aged under atmospheric air, the NIST library match [14], and Butyl #10 aged under an $^{18}O_2$ enriched environment were compared and shifts in the molecular ion ($M^{+\bullet}$) that related to isotopic enrichment (+2 Da for each O-18 label) were noted.

After noting isotopic shifts in the molecular ion peak, predictable fragmentation schemes [13] were mapped based on the NIST mass spectral library matches [14]. Combining these fragmentation schemes with mass spectral shifts in the fragment ion peaks allowed us to pinpoint which fragments in the molecule contained an isotopic label. Cases in which small fragment ion peaks (≤ ~5% of the base peak intensity) may have been indicative of another isotopic labeling position were considered to be insignificant since they were likely within the expected limits of error for the cryo-GC/MS instrumentation (e.g., in the mass spectral noise). Ultimately, we were able to identify an O-18 label and verify its presence in the predicted oxygen containing fragment ion(s) for each applicable compound detected, as indicated in Table 8.

Eleven of the nineteen total degradation products detected for samples of Butyl #10 aged under an $^{18}O_2$ enriched atmosphere contained oxygen atoms: acetaldehyde **{2}**, methyl alcohol **{4}**, acetone **{5}**, tert-butyl alcohol **{6}**, 2-methyl propanal **{7}**, 2,2-dimethyl propanal **{8}**, 2-butanone **{9}**, 2-pentanone **{12}**, 4,4-dimethyl-2-pentanone **{15}**, 2,4-dimethyl-3-pentanone **{16}**, and tetrahydro-2,2,4,4-tetramethyl-furan **{17}**. Seven of the remaining eight species were alkenes (2-methyl-1-propene **{1}**, 2,4-dimethyl-1-pentene **{10}**, 2,4-dimethyl 1,4-pentadiene **{11}**, 2,4,4-trimethyl-1-pentene **{13}**, *2,4,4-trimethyl-2-pentene* ***{14}***, *3,5,5-trimethyl-2-hexene* ***{18}***, and 2,4,4-trimethyl-1-hexene **{19}**). The final species detected was identified as bromomethane **{3}**, which is related to Lanxess bromobutyl 2030 Butyl #10 starting material.

For all oxygenated products but tetrahydro-2,2,4,4-tetramethyl-furan **{17}**, amounts of both unlabeled and isotopically labeled $M^{+\bullet}$ were seen in the mass spectra where contributions from the $^{18}O_2$ enriched atmosphere were relatively small compared to those from an O-16 oxygen atom source. In other words, the aging environment was 99% $^{18}O_2$ enriched, but the relative percentage of product that formed by way of $^{16}O_2$ or $^{18}O_2$ did not correlate to this ratio. Those species containing O-16, as noted by the lack of a complete +2 Da shift in the mass spectra, must have formed from an oxygen source other than the aging environment. Sources for O-16 atoms may include but are not limited to: polyethylene AC-616 Butyl #10 additive, zinc oxide Butyl #10 activator, Vanax MBM Butyl #10 additive, an unexpected contaminant, or oxygen that was not removed from the aging vessel or present in the gas cylinder of enriched $^{18}O_2$. The details surrounding the identification of an O-18 label for two compounds (acetone **{5}** and tetrahydro-2,2,4,4-tetramethyl-furan **{17}**) will be discussed herein.

The NIST library mass spectrum [14] for acetone **{5}** along with the mass spectrum corresponding to the GC peak identified as acetone **{5}** in samples of Butyl #10 aged in ambient air (109 °C for 60 total days) and under an $^{18}O_2$ enriched environment (109 °C for 61 total days) as well as the proposed acetone **{5}** fragmentation pathway [13] are depicted in Figure 8. The +2 Da shift for the molecular ion at *m/z* 58 ($[C_3H_6O]^{+\bullet}$) along with a fragment ion that formed after a methyl radical ($[CH_3]^{\bullet}$) loss at *m/z* 43 ($[C_2H_3O]^{+}$) indicated one O-18 atom was present in the molecular structure, as expected given acetone **{5}** contains only one oxygen atom. The lack of a shift for the ion at *m/z* 15 ($[CH_3]^{+}$) that formed by way of a subsequent loss of carbon monoxide (CO) from the fragment ion assigned to *m/z* 43 agreed with our predictions.

Similarly, the NIST library mass spectrum [14] for tetrahydro-2,2,4,4-tetramethyl-furan **{17}** along with the mass spectrum corresponding to the GC peak identified as tetrahydro-2,2,4,4-tetramethyl-furan **{17}** in samples of Butyl #10 aged in ambient air and under an $^{18}O_2$ enriched environment (109 °C for 30 total days) as well as the proposed tetrahydro-2,2,4,4-tetramethyl-furan **{17}** fragmentation pathway [13] are depicted in Figure 9. Though the molecular ion for this compound (*m/z* 128 $[C_8H_{16}O]^{+\bullet}$) was not stable enough to be detected by the mass spectrometer, several fragment ions were. Following a rearrangement, the ions at *m/z* 70 ($[C_5H_{10}]^{+\bullet}$), 55 ($[C_4H_7]^{+}$), and 27 ($[C_2H_3]^{+}$) correlate to subsequent losses of acetone (C_3H_6O), $[CH_3]^{\bullet}$, and ethene (C_2H_4), respectively. Similarly, a loss of formaldehyde (CH_2O) and $[CH_3]^{\bullet}$ results in the formation of the ion at *m/z* 83 ($[C_6H_{11}]^{+}$). An initial loss of $[CH_3]^{\bullet}$ from the molecular ion produces the oxygen containing ion at *m/z* 113 ($[C_8H_{16}O]^{+\bullet}$). Starting with the ion at *m/*z 113, ions at *m/z* 59 ($[C_3H_7O]^{+}$) and 43 ($[C_2H_3O]^{+}$) form by either a loss of C_4H_6 or C_5H_{10}, respectively. These three ions (*m/z* 113, 59, and 43) all contain oxygen atoms and exhibit a +2 Da shift in the respective mass spectrum (Figure 9c). In fact, there was no contribution from O-16 atoms for these ions. This suggests that tetrahydro-2,2,4,4-tetramethyl-furan **{17}** is formed completely from oxygen in the aging environment unlike the other oxygenated degradation species of Butyl #10. The remaining two ions form by way of a loss of water (*m/z* 95 $[C_7H_{11}]^{+}$) or $C_6H_{10}O$ (*m/z* 15 $[CH_3]^{+}$, two pathways) from *m/z* 113 and did not show a shift in mass number, as expected.

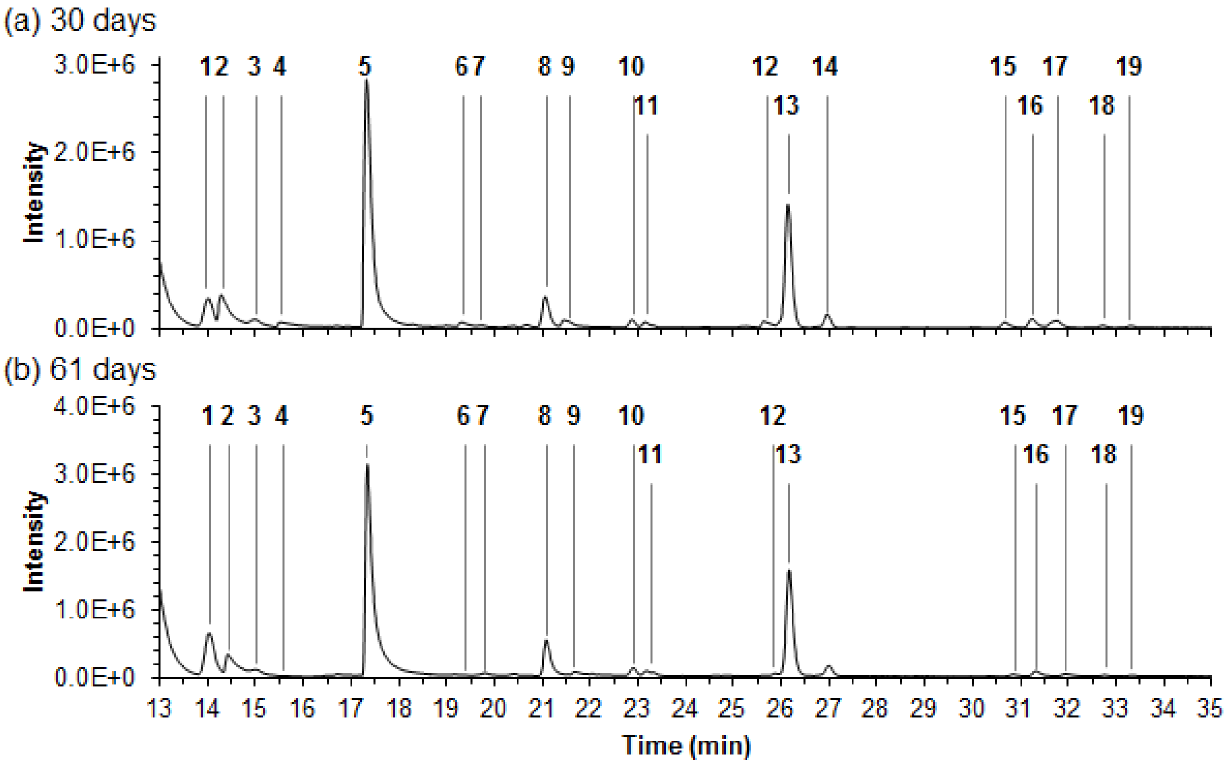
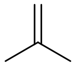
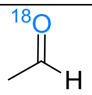


Figure 7. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Butyl #10 aged under an oxygen-18 (O-18) enriched environment at 109 °C for (a) 30 and (b) 61 total days in series. The numbers 1-19 across the top of the chromatograms correspond to the identified degradation products as listed in Table 8.

Table 8. Low-molecular weight volatile Butyl #10 thermal-oxidation degradation products originating from samples aged under an oxygen-18 (O-18) enriched environment for up to 61 total days in series at 109 °C[a]



2-methyl-1-propene **{1}**
(C_4H_8, 56.0626)



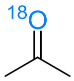
acetaldehyde **{2}**
(C_2H_4O, 44.0262)

CH_3Br

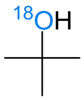
bromomethane **{3}**
(CH_3Br, 93.9418)

$-{}^{18}OH$

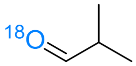
methyl alcohol **{4}**
(CH_4O, 32.0262)



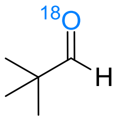
acetone **{5}**
(C_3H_6O, 58.0419)



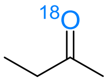
tert-butyl alcohol **{6}**
($C_4H_{10}O$, 74.0732)



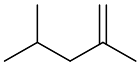
2-methyl propanal **{7}**
(C_4H_8O, 72.0575)



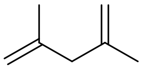
2,2-dimethyl propanal **{8}**
($C_5H_{10}O$, 86.0732)



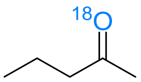
2-butanone **{9}**
(C_4H_8O, 72.0575)



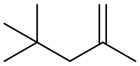
2,4-dimethyl-1-pentene **{10}**
(C_7H_{14}, 98.1096)



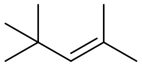
2,4-dimethyl 1,4-pentadiene **{11}**
(C_7H_{12}, 96.0939)



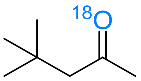
2-pentanone **{12}**
($C_5H_{10}O$, 86.0732)



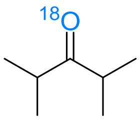
2,4,4-trimethyl-1-pentene **{13}**
(C_8H_{16}, 112.1252)



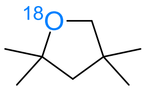
2,4,4-trimethyl-2-pentene ***{14}***
(C_8H_{16}, 112.1252)[b]



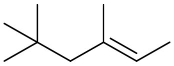
4,4-dimethyl-2-pentanone **{15}**
($C_7H_{14}O$, 114.1045)



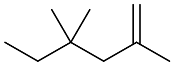
2,4-dimethyl-3-pentanone **{16}**
($C_7H_{14}O$, 114.1045)



tetrahydro-2,2,4,4-tetramethyl-furan **{17}**
($C_8H_{16}O$, 128.1201)[c]



3,5,5-trimethyl-2-hexene ***{18}***
(C_9H_{18}, 126.1409)[d]



2,4,4-trimethyl-1-hexene **{19}**
(C_9H_{18}, 126.1409)

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[a] Compounds are numbered by increasing retention time (see Figure 7). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product. *Compound names* have been italicized for cases where it was difficult to assign specific structural isomers and the best match has been pictured in the table.

[b] *Structural assignment:* trimethyl-pentene variation

[c] Unlike every other oxygenated degradation product, the molecular ion and applicable fragment ions for this species were composed of all O-18 labeled oxygen atoms (i.e., no O-16 atoms were present).

[d] *Structural assignment:* trimethyl-hexene variation, might be 2,5,5-trimethyl-2-hexene

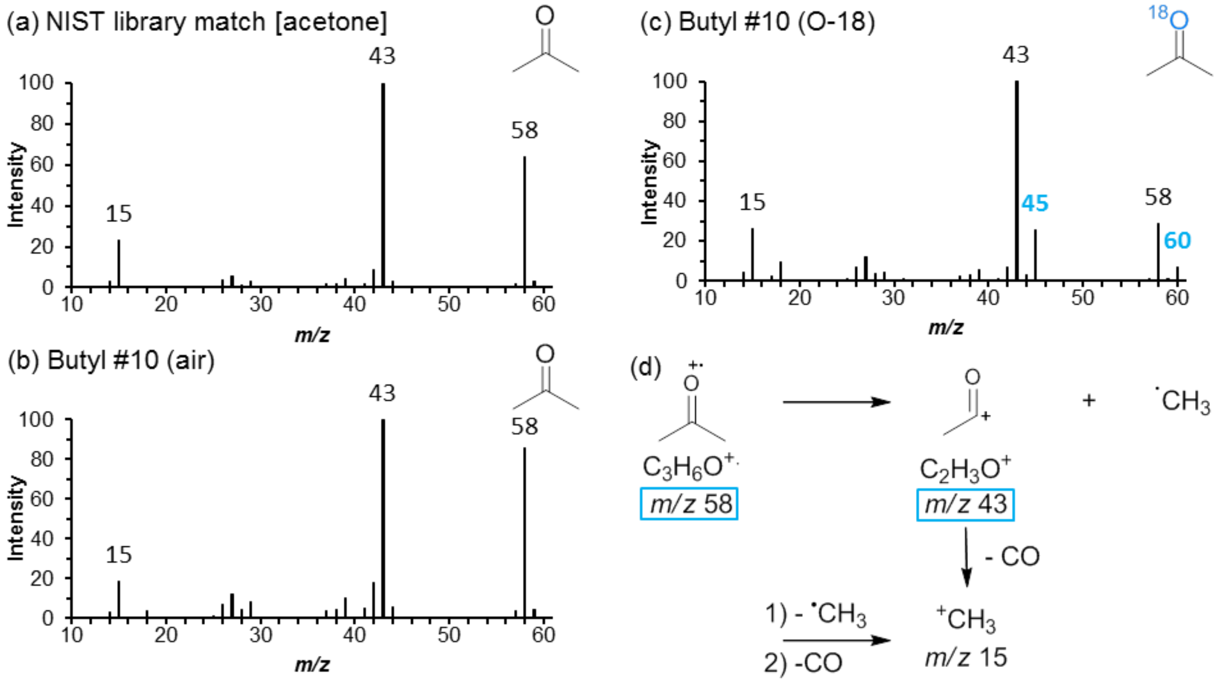


Figure 8. The (a) NIST mass spectrum [14] for acetone {5} along with the mass spectrum from Butyl #10 aged at 109 °C for (b) 60 total days under oxidative conditions and (c) 61 total days under an oxygen-18 (O-18) enriched environment were compared to determine if the degradation species contained an O-18 label. The (d) proposed ion fragmentation pathway for acetone {5} tracks the location for the O-18 atom. The “blue boxes” and “blue text” indicate a +2 Da shift was seen in the mass spectrum comparison.

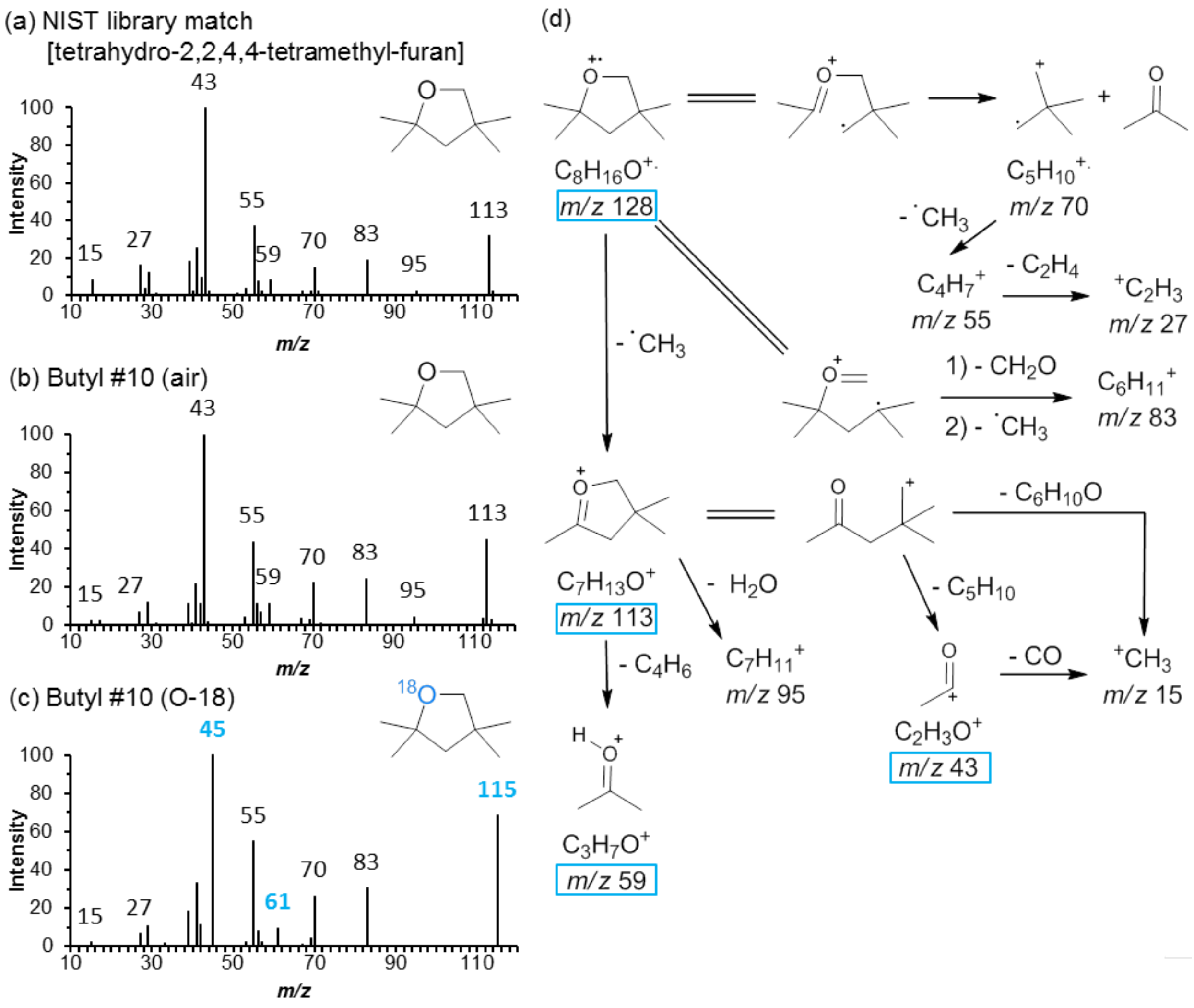


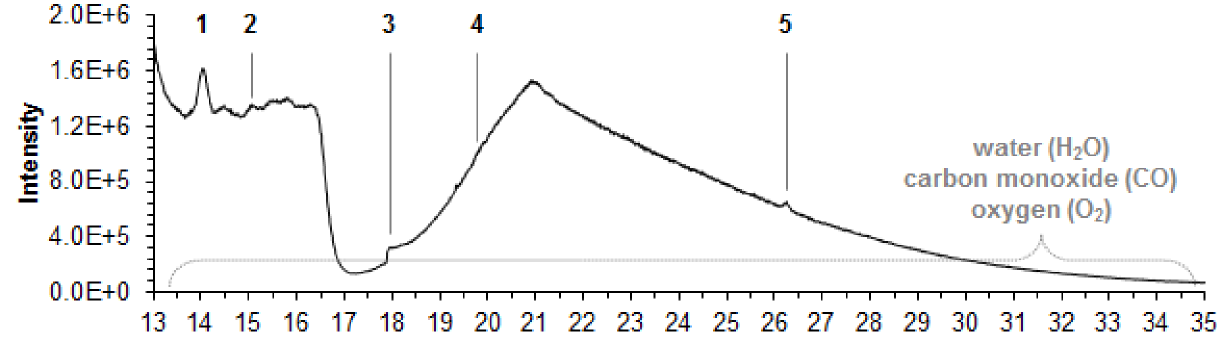
Figure 9. The (a) NIST mass spectrum [14] for tetrahydro-2,2,4,4-tetramethyl-furan {17} along with the mass spectrum from Butyl #10 aged for 30 total days at 109 °C under (b) oxidative conditions and (c) an oxygen-18 (O-18) enriched environment were compared to determine if the degradation species contained an O-18 label. The (d) proposed ion fragmentation pathway for tetrahydro-2,2,4,4-tetramethyl-furan {17} tracks the location for the O-18 atom. The "blue boxes" and "blue text" indicate a +2 Da shift was seen in the mass spectrum comparison.

3.3.5. Argon Atmosphere

Five volatile compounds were present in the headspace above duplicate samples of Butyl #10 aged under an argon environment for 30 and 92 totals days in series at 109 °C (Figure 10 and Table 9). The detection -of two alkenes (2-methyl-1-propene **{1}** and 2,4,4-trimethyl-1-pentene **{5}**) and bromomethane **{2}** was not surprising since all three of these species relate back to the polymeric structure of Butyl #10. However, the appearance of two oxygenated degradation species (acetone **{3}** and tert-butyl alcohol **{4}**), along with three oxygenated compounds present throughout the background (water, carbon monoxide, and oxygen), was not expected.

Background subtraction was needed in order to determine acetone **{3}** and tert-butyl alcohol **{4}** were present, which suggests they may have been contaminant/impurity or formed using very small amounts of oxygen present in the system. Water was seen throughout the chromatogram and accounted for ~80% of the total signal intensity, which confirms how difficult it is to remove all of water from the system. Carbon monoxide and oxygen were detected at levels near the instrument noise (~0.5% of the total signal intensity). Thus, these experiments have been deemed not to occur under entirely non-oxidative thermal degradation conditions but were rather conducted under slightly thermal-oxidative conditions. It is also worth noting that after 92 total days of aging, the drastic drop in signal intensity suggests that only a very small amount of 2-methyl-1-propene **{1}** and water were present *vs.* the quantities present at 30 total days of aging. Nonetheless, comparing this set of experiments (Figure 10) to those for Butyl #10 in ambient air (Figure 3) did confirm the claim [16] that degradation of butyl rubber is much more extensive in air than argon.

(a) 30 days



(b) 92 days

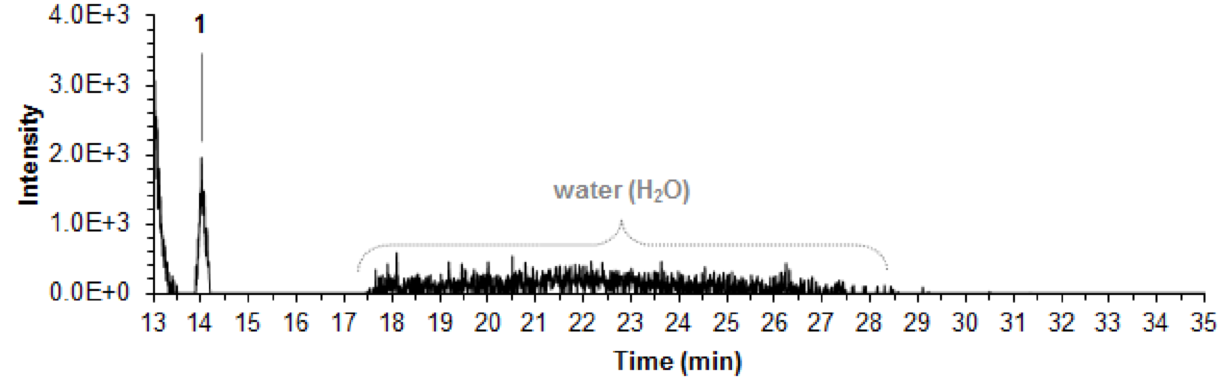
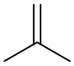
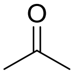
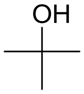
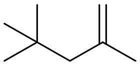


Figure 10. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Butyl #10 aged under an argon environment at 109 °C for (a) 30 and (b) 92 total days in series. The numbers 1-5 across the top of the chromatograms along with the other labeled species correspond to the identified degradation products as listed in Table 9.

Table 9. Low-molecular weight volatile Butyl #10 non-oxidative thermal degradation products originating from samples aged under an argon environment for up to 92 total days in series at 109 °C[a]

 2-methyl-1-propene **{1}** (C_4H_8, 56.0626)	CH_3Br bromomethane **{2}** (CH_3Br, 93.9418)	 acetone **{3}** (C_3H_6O, 58.0419)	 tert-butyl alcohol **{4}** ($C_4H_{10}O$, 74.0732)
 2,4,4-trimethyl-1-pentene **{5}** (C_8H_{16}, 112.1252)	H_2O water (H_2O, 18.0106)	$^+O{\equiv}C^-$ carbon monoxide (CO, 27.9949)	O=O oxygen (O_2, 31.9898)

[a] Compounds are numbered by increasing retention time (see Figure 10). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product.

3.4. Butyl #21

Thirteen volatile compounds were present in the headspace of duplicate samples of Butyl #21 aged under ambient air for 30 and 61 totals days in series at 109 °C (Figure 11 and Table 10). One alkane (2,2,4-trimethyl-pentane **{10}**) and six alkenes (2-methyl-1-propene **{1}**, 2,4-dimethyl-1-pentene **{7}**, 2,4-dimethyl-2-pentene **{8}**, 2,4-dimethyl 1,4-pentadiene **{9}**, 2,4,4-trimethyl-1-pentene **{11}**, and 2,4,4-trimethyl-2-pentene **{13}**) encompassed the identified species representing the hydrocarbon family. The five compounds containing oxygen atoms included: alcohols (methyl alcohol **{2}** and tert-butyl alcohol **{5}**), ketones (acetone **{3}** and 3,3-dimethyl-2-butanone **{12}**), and an aldehyde (2,2-dimethyl propanal **{6}**). Carbon disulfide **{4}** was also detected in large amounts and is most likely linked to the sulfur containing thiocarbamate accelerator [17] (Advance 5364 ZDMC Pellets-80 (zinc dimethyldithiocarbamate)) that was used in the Butyl #21 formulation (Table 1).

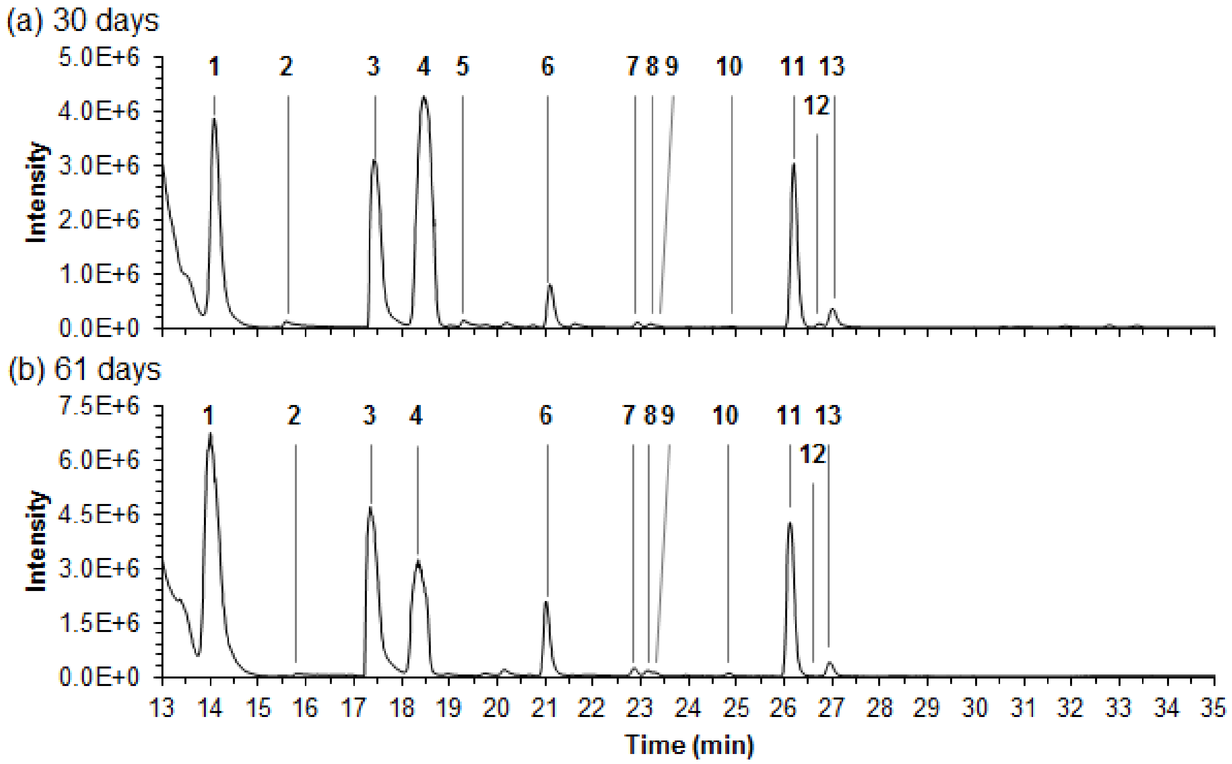
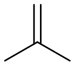


Figure 11. Gas chromatograms of the total ion current (TIC) *vs.* time for the gaseous species that accumulated in the headspace over Butyl #21 aged under an ambient atmosphere at 109 °C for (a) 30 and (b) 61 total days in series. The numbers 1-13 across the top of the chromatograms correspond to the identified degradation products as listed in Table 10.

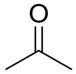
Table 10. Low-molecular weight volatile Butyl #21 thermal-oxidation degradation products originating from samples aged under oxidative conditions for up to 61 total days in series at 109 °C[a]



2-methyl-1-propene **{1}**
(C_4H_8, 56.0626)

—OH

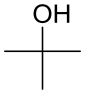
methyl alcohol **{2}**
(CH_4O, 32.0262)



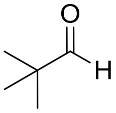
acetone **{3}**
(C_3H_6O, 58.0419)

S=C=S

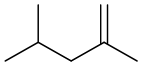
carbon disulfide **{4}**
(CS_2, 75.9441)



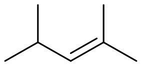
tert-butyl alcohol **{5}**
($C_4H_{10}O$, 74.0732)



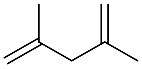
2,2-dimethyl propanal **{6}**
($C_5H_{10}O$, 86.0732)



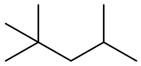
2,4-dimethyl-1-pentene **{7}**
(C_7H_{14}, 98.1096)



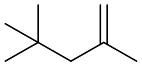
2,4-dimethyl-2-pentene **{8}**
(C_7H_{14}, 98.1096)



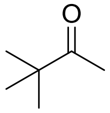
2,4-dimethyl 1,4-pentadiene **{9}**
(C_7H_{12}, 96.0939)



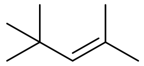
2,2,4-trimethyl-pentane **{10}**
(C_8H_{18}, 114.1409)



2,4,4-trimethyl-1-pentene **{11}**
(C_8H_{16}, 112.1252)



3,3-dimethyl-2-butanone **{12}**
($C_6H_{12}O$, 100.0888)



2,4,4-trimethyl-2-pentene **{13}**
(C_8H_{16}, 112.1252)

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[a] Compounds are numbered by increasing retention time (see Figure 11). Chemical structures, molecular formulas, and the exact masses (Da) are listed for each degradation product.

3.5. Comparison of Butyl Formulations

Almost all of the thermal-oxidative degradations products described in the above text for Butyl #6, #10, and #21 along with the Butyl #10 related materials were alkanes, alkenes, alcohols, ketones, and aldehydes. Though the exact structure for all of the hydrocarbons was not clear, we have determined that the majority of detected hydrocarbons were alkenes. Other authors have suggested that these thermal-oxidative degradation species form by way of radical and macroradical formation that result from oxygen attack of the butyl rubber's isoprene units [10, 11]. These radicals can participate in chain scission and combine in cross-linking reactions, which can lead to the formation of oxygenated products [10]. Cross-linking has been identified as the dominant oxidation mechanism for halobutyl elastomers [10], such as those studied here. Ketone, aldehyde, and acid groups can form by way of a disproportionality of hydroxyl and alkoxy radicals followed by oxidation and chain breaking [10]. Similarly, the decomposition of hydroperoxides has been shown to yield alkoxy radicals and the subsequent formation of ketones and aldehydes ensuing chain scission [10].

To demonstrate the potential role of peroxide formation in the degradation of butyl rubber, a neat sample of one of the most stable peroxides (tert-butyl hydroperoxide) was analyzed using cryo-GC/MS under the sample conditions described in the experimental section of this manuscript. Retention times, mass spectral fingerprints, and mass spectral library matching [14] was used to identify the detected products (data not shown) as compared to those recorded for the thermal-oxidative degradation species of the butyl rubber formulations, starting material, and additives. The five chemicals that were also detected in the aged samples were: 2-methyl-1-propene, methyl alcohol, acetone, tert-butyl alcohol, and 2-butanone. Though this was not an extensive study, the results do confirm that peroxide formation may play a significant role in the degradation of butyl rubbers [9].

When comparing the degradation species for Butyl #10 starting material and additives to that of Butyl #10, we see many of same species or very similar ones. The differences are likely due to the fact that the starting materials and additives are only one compound whereas Butyl #10 is a complex formulation of many chemical ingredients. That is, there are more compounds available for potential chemical reactions in the aged samples of Butyl #10. This seemingly results in more and different thermal-oxidative degradation products and reaction pathways for the multifaceted polymeric mixture.

4. CONCLUSIONS

Small quantities of low-molecular weight volatile compounds that collected in the headspace over aged samples (up to 413 total days at up to 124 °C) of two in-house butyl rubber formulations (#6 and #10) and one commercially available formulation (#21) were identified using cryofocusing gas chromatography mass spectrometry (cryo-GC/MS). Degradation species of Butyl #10 starting material (Laxness bromobutyl 2030) and two additives (polyethylene AC-617 and Vanax MBM) were also investigated. A comparison of all GC chromatograms showed good alignment of all decomposition products and indicated that species gradually decreased in quantity as aging time progressed (i.e., the polymeric material degraded). A comparison of mass spectra and ion fragmentation pathways for Butyl #10 and Butyl #10 aged in isotopically enriched oxygen ($^{18}O_2$) aided in determining the exact number of the isotopically labeled atom(s) in oxygenated degradation products. This information was also used to determine the source of the oxygen in the degradation products (i.e., an addition, contaminate, the aging environment, *etc.*). A sample of Butyl #10 was also aged in an argon atmosphere, and the products that formed by way of a non-oxidative thermal degradation pathway were compared to those formed by thermal-oxidative degradation of the elastomer. The detected degradation species were mostly alkanes, alkenes, alcohols, ketones, and aldehydes, which agreed well with the literature [9-11]. However, carbon disulfide, likely a sulfur impurity, was detected for samples of Butyl #10 aged for 413 total days.

4.1. Future Work

A few samples of Butyl #10 are currently undergoing a long term aging study. Aging of the samples began on 03-16-2010 under an ambient atmosphere at 80 and 64 °C. In July of 2012, the samples had aged for roughly 850 days and were predicted to have ~70% (80 °C) and ~80% (64 °C) of their compression strength remaining [6]. In the future, the headspace above these materials will be sampled; the degradation species will be characterized; and comparisons will be drawn to samples presented in this manuscript. In addition, these results and those for other polymers can be compared to compounds of interest to the DOE complex that have already been studied by this group: polyethylene [18, 19], polypropylene [20-22], nylon 6.6 [23-26], and poly(ethylene-co-vinyl acetate). This information may identify common degradation products and therefore degradation pathways amongst WR materials. Possible contamination of the starting materials (e.g., sulfur in Butyl #10) could be investigated using elemental analysis. The effect of varying humidity levels on butyl rubber and other polymers could also be examined, which may identify conditions that severely degrade or strengthen the material.

One disadvantage to these studies was that they were not quantitative, typically accomplished by using a known standard for which to normalize gas chromatogram areas for each distinguishable peak. That information could be used to make comparisons across all samples at various aging times and temperatures. Consequently, conclusions regarding the relative amount of each degradation species formed and how that correlates to the degrading polymer’s lifetime could be drawn.

Knowing the location for specifically designed butyl rubber materials containing isotopically labeled atoms would allow us to us to map individual degradation compounds onto the polymeric structure and determine the mechanisms used to form each specific species. Further, an understanding of the complex degradation mechanisms of butyl rubber and specific quantities or each degradation species under certain conditions could be used to create chemical sensors that detect and monitor a specific chemical(s) that outgases as the polymer ages and thus a change occurs in the physical properties (e.g., loss compression strength). Quantitative information determined by a sensor for a given degradation product could also be used to determine if the polymeric material is still viable without having to test it with destructive methodologies.

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