

Thermal Decomposition Kinetics of Polyol Ester Lubricants[†]

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Abstract

Synthetic lubricants are widely used for applications that require high thermal and oxidative stability. In order to facilitate new designs and applications for these fluids we are measuring a suite of thermophysical and transport properties for lubricant base fluids and mixtures. As part of the property measurements, here we report the global thermal decomposition kinetics of four polyol ester lubricant base oils, in addition to a fully qualified (MIL-PRF-23699) formulation. The fluids were heated in stainless steel ampule reactors and the extent of decomposition was measured by gas chromatography (GC) with flame ionization detection, from which pseudo-first-order rate constants were derived. The rate constants for decomposition ranged from $1 \times 10^{-8} \text{ s}^{-1}$ at 500 K to $2 \times 10^{-4} \text{ s}^{-1}$ at 675 K. Arrhenius parameters across this temperature regime are also reported. Other techniques for chemical characterization applied in this work include GC with mass spectrometry, NMR spectroscopy, and Karl Fischer titration.

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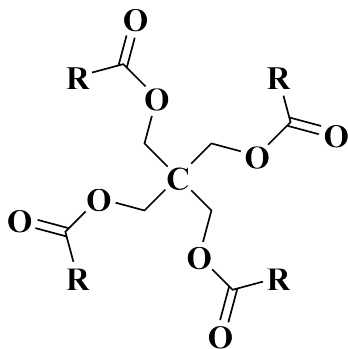
Introduction

Polyol ester based lubricants have been used since the late 1930s and are now some of the most common synthetic lubricants available today.¹ Their use extends over many industries and applications, including aircraft turbine engines, hydraulic fluids, refrigeration, and textiles. Though they are generally more expensive than hydrocarbon-based lubricants, they offer more consistent physical properties and biodegradability than mineral oils. Polyol ester lubricants also have better thermal and oxidative stability in addition to lower volatility, which results in longer lifetimes at higher temperatures and reduced consumption.^{2,3}

The physical and chemical properties of these fluids are of particular interest to the aviation community, because polyol esters are the preferred base stock for the lubrication of aircraft turbine engines.^{1,4} As components aboard the aircraft evolve and approach more extreme environments it is critical to predict how the fluid will behave for new designs and applications. The thermophysical properties (thermodynamic and transport) that are needed include density, vapor pressure, heat capacity, sound speed, viscosity, and thermal conductivity. Some property measurements have already been performed on polyol ester base oils and lubricants,⁵⁻⁸ in addition to mixtures for refrigeration applications.⁹ Additional measurements are being performed at NIST to expand the temperature and pressure regimes and provide updated thermophysical property models.¹⁰⁻¹²

Although neopentyl polyol esters are considered to be more thermally stable than other esters, attributed to the absence of a labile hydrogen on the β -carbon (central carbon atom in Figure 1), they are not immune to thermal degradation. Prior to performing the thermophysical property measurements mentioned above, we need to assess the fluid's thermal stability to determine optimal operating conditions to ensure measurements are made on the species of interest (i.e. not the decomposition products) and protect instrumentation from potential upset conditions and decomposition products. The thermal decomposition measurements are performed in stainless steel ampule reactors, and the extent of decomposition, as a function of time, is determined by gas chromatography (GC) with flame ionization

detection (FID). Similar measurements have been performed on pure fluids¹³ and fuel mixtures¹⁴⁻¹⁷ employing this strategy. From these measurements, rate constants and ultimately Arrhenius parameters can be determined which provide a guide for the subsequent property measurements and in-service constraints.



pentaerythritol tetrapentanoate (PEC5): $R = n\text{-C}_4\text{H}_9$
 pentaerythritol tetraheptanoate (PEC7): $R = n\text{-C}_6\text{H}_{13}$
 pentaerythritol tetranonanoate (PEC9): $R = n\text{-C}_8\text{H}_{17}$
 pentaerythritol tetra-3,5,5-trimethyl hexanoate (PEB9): $R = i\text{-C}_8\text{H}_{17}$

Figure 1: Chemical structure and nomenclature of the pentaerythritol tetraesters studied

In general, the decomposition of these large molecules is complex, involving the formation of vapors, liquids, and solids. There have been numerous studies on the oxidative decomposition of polyol ester lubricants, including proposed oxidation pathways,^{2,3,18-20} routes for the formation of polymers,^{21,22} in addition to measured global oxidation rates.^{3,19} Lower molecular weight decomposition products and gases that have been detected in these studies include carbon monoxide, carbon dioxide, paraffins, aldehydes, methyl ketones, carboxylic acids, and methyl esters of carboxylic acids, in addition to some olefins and alcohols. Larger, liquid-phase oxidation products from these tetraesters include tri-esters that are aldehyde, acid, or hydrogen terminated.^{23,24} In one study by Wang *et al.*, the volatiles were monitored by GC with mass spectrometry (MS) while simultaneously measuring the solid, polymeric deposits with a quartz crystal microbalance.³

Several studies have also shown that the polyol ester thermal degradation is enhanced by catalytic surface reactions.²⁵⁻²⁹ Kauffman, in particular, provides excellent reviews on the

subject of metal/metal oxide reactions with polyol ester lubricants at elevated temperatures, specifically as they relate to esters in the presence of refrigerants.^{26,27} Metals and metal oxides that were found to catalyze the decomposition of pentaerythritol tetrapentanoate (PEC5) were Fe, Fe(II) oxide, Sn, and Zn. The presence of water and impurities due to incomplete esterification of the starting polyol also contribute to catalytic decomposition in the presence of metal surfaces. Formulation improvements with additives have been employed to help address some of these issues.^{25,28} An important additive for polyol ester lubricants is tricresyl phosphate (TCP), which forms a layer on metallic surfaces, separating the base oil from the metal, thereby reducing decomposition associated with the interaction.³⁰

As part of the suite of thermophysical property measurements being measured at NIST, in this paper we report the global thermal decomposition kinetics of four polyol ester lubricant base oils (see Figure 1), in addition to a fully qualified (MIL-PRF-23699) formulation. All pure fluids are pentaerythritol-based with the esters pentanoate (PEC5), heptanoate (PEC7), nonanoate (PEC9) or 3,5,5-trimethylhexanoate (PEB9). The qualified lubricant is a proprietary blend of pentaerythritol polyol esters in the C₅ to C₁₀ range, in addition to TCP for surface passivation and a selection of aliphatic amines to prevent hydrolytic degradation and neutralize TCP-derived acids.²⁵ Measurements of these fluids were performed over a range of temperatures and analyzed by GC with FID in order to develop Arrhenius expressions. Other techniques used for chemical characterization include GC with mass spectrometry (MS), NMR spectroscopy, and Karl Fischer titration. Accelerated tests of PEC9 in the presence of select materials were also performed to assess the potential catalytic behavior of the polyol esters.

Experimental Methods

Thermal Decomposition Rate Analysis

Thermal decomposition of polyol esters, whether a pure component fluid or a mixture, is a complex process. Each component has multiple decomposition routes available and further decomposition of the initial set of products can also occur. Due to this complexity, it is necessary to make assumptions in order to simplify the analysis and determine rate expressions to describe the thermal stability of these fluids. We assume that the reactant of interest, A, thermally decomposes to a set of products and that we can model the overall decomposition with a single, global pseudo-first-order rate constant, k' .

Since the product suite contains both hydrocarbons and oxygenated species, quantitative analysis by flame ionization detection (FID) of the product suite is complicated because the detector has a variable response to the amount of oxygen present. In order to avoid calibrating the FID response for all possible product species, we instead monitor the disappearance of the reactant(s), $[A]_t$, relative to the products formed, and compare this to an unheated reference sample, $[A]_0$, to measure the ‘unreacted fraction’:

$$\ln \frac{[A]_t}{[A]_0} = \ln(\text{unreacted fraction}) = -k't \quad (1)$$

The rate constant, k' , at a particular temperature is derived from Eq. 1, in a plot of $\ln(\text{unreacted fraction})$ *vs.* reaction time. From here, $t_{0.5}$ (half-life) and $t_{0.01}$ (time required for 1 % of the fluid to thermally decompose) are calculated to help guide the subsequent property measurements.

We also assume that analysis of only the remaining liquid fraction of the decomposed fluid is representative of the decomposition process. Based on our observations, the extent of decomposition that ensures that this is a valid assumption is at most 40 %. Additional decomposition beyond this point results in a significant vapor phase (which is not quantita-

tively analyzed for all experiments) and serves as an indication that the initial set of products are undergoing thermal decomposition. Analysis of samples with more than 40 % of reactant decomposed will also not fall on a straight line with the less decomposed samples in a plot of Eq. 1, which is an indication of where the pseudo first-order approximation begins to break down.

Finally, the rate constants are measured over a range of temperatures to develop an Arrhenius expression to describe the fluid’s thermal stability based on the activation energy, E_a (in J mol⁻¹) and the pre-exponential factor, A (units of s⁻¹):

$$k'(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the reaction temperature. The validity of this analysis scheme for low-temperature decomposition of RP-1¹⁴ has been corroborated by shock tube measurements at much higher temperatures,³¹ showing excellent agreement in the Arrhenius fit of the data across a temperature range of about 600 K.

Chemicals

The straight-chain neopentyl polyol ester base oils, pentaerythritol tetrapentanoate (PEC5), tetraheptanoate (PEC7,) and tetranonanoate (PEC9) were obtained from a commercial supplier and experiments conducted within one year from the date of manufacture. A branched polyol ester base oil, containing primarily pentaerythritol tetra-3,5,5-trimethylhexanoate (PEB9), was also tested; this sample was manufactured over 15 years prior to the thermal decomposition experiments. The fully qualified lubricant (referred to here as ‘lubricant’ or ‘mixture’) meets the military performance specification for aviation turbine engines, MIL-PRF-23699.³² The lubricant was prepared by the manufacturer by co-esterification of pentaerythritol with several monobasic fatty acids, both straight chain and branched, resulting in a complex mixture of unique polyol esters to produce the desired properties of the final

mixture.^{33,34} The lubricant also contains additives to improve thermal stability, corrosion resistance, and hydrolytic degradation (approximate concentrations (by mass) from specifications: tricresyl phosphate (1 % to 5 %), assorted amines/naphthylamines (0.1 % to 1 %)).

The purity of the base oils was determined by GC-FID, GC-MS, and ¹³C NMR; the results from these methods are summarized in Table 1. Purity determinations of these esters by NMR spectroscopy are hampered by overlap between the pentaerythritol ester peaks and impurity peaks. For these compounds, the best separation between the primary peak and associated impurity peaks was observed for the central (quaternary) carbon atom, which resonates at a chemical shift of about 42 ppm. This type of purity determination will only account for impurities that contain the pentaerythritol moiety (such as pentaerythritols that are not fully esterified, or that are esterified with different fatty acids). Consequently, the purities for the linear esters should be viewed as upper limits, and the actual purities could be lower. Based on this type of analysis, the mole fraction purities of the pentaerythritol esters are shown in Table 1, and the uncertainty estimates are the combined expanded (coverage factor of 2) uncertainties based on an assessment of relaxation and nuclear Overhauser effects, detection limits, baseline drift, and peak overlap. Expanded uncertainty estimates for GC-FID are based upon statistical sampling uncertainty in addition to an estimate of uncertainty for the complete separation of components in the mixtures.

Also shown in Table 1 are the major impurities in the base oil samples detected by GC-MS. Impurities were primarily fully esterified polyol esters with tails of different chain lengths, as determined by their ion fragmentation patterns by GC-MS³⁵⁻³⁷ and discussed in more detail in the Results section. Approximately 0.1 % to 0.7 % of uncalibrated FID peak area are triesters with a single –OH terminal group; estimated mol % of these impurities are also included in Table 1. All fluids were used as received from suppliers; no additional purification or drying of the oils were performed prior to the thermal decomposition measurements.

Table 1: Purity Analysis of Base Oils and Fully Qualified Lubricant

Fluid	Formula	CAS	Molar Mass	GC-FID	^{13}C NMR	H ₂ O Content		acyl moiety impurities	tri-ester mol %
				mol % purity	mol % purity	$\mu\text{g g}^{-1}$	mol %		
PEC5	C ₂₅ H ₄₄ O ₈	15834-04-5	472.6	96.7 ± 0.2	< 99.2 ± 0.6	500 ± 20	1.3	C ₄ <i>b</i> -C ₅ C ₇ C ₈ C ₉	0.4
PEC7	C ₃₃ H ₆₀ O ₈	25811-35-2	584.8	97.3 ± 0.8	< 98.5 ± 0.8	420 ± 20	1.4	C ₅ C ₆ C ₈	< 0.1
PEC9	C ₄₁ H ₇₆ O ₈	14450-05-6	697.0	93.0 ± 1.0	< 97.3 ± 1.0	240 ± 20	0.93	C ₆ C ₇ C ₈ C ₁₀	0.1
PEB9	C ₄₁ H ₇₆ O ₈	41058-87-1	697.0	72.3 ± 2.0	62.7 ± 9.0	275 ± 20	1.1	C ₅ thru C ₁₀	0.7
lubricant	N/A	N/A	564.9*	N/A	N/A	270 ± 20	0.87	–	–

*average value based on polyol ester mixture composition determined by ^{13}C NMR³⁸

Acetone and toluene (HPLC grade, ≥ 99.9 %, mass/mass), obtained from commercial suppliers, were used as received to clean the reactors and valve components following each experiment. Samples of the base oils (unheated and thermally decomposed) were diluted with either *n*-dodecane (anhydrous, ≥ 99 %, mass/mass) or *n*-decane (anhydrous, ≥ 99 %, mass/mass) for analysis by GC-FID or GC-MS. The carrier gases for GC with FID and MS were nitrogen (research grade) and helium (ultra high purity), respectively.

Sample Analysis by ^{13}C and ^1H NMR Spectroscopy

A commercial 600 MHz nuclear magnetic resonance (NMR) spectrometer with a cryoprobe, operated at 150.9 MHz for ^{13}C , was used to obtain all of the ^{13}C spectra. Samples for ^{13}C NMR spectroscopy were prepared by mixing 0.25 g of a pentaerythritol ester with 1 g of chloroform-*d* (which contained 0.05 % by volume of the chemical shift reference TMS). Samples for ^1H NMR spectroscopy were prepared by mixing (10 to 20) mg of pentaerythritol ester with 1 g of chloroform-*d* (which also contained 0.05 % by volume of the chemical shift reference TMS). The samples were maintained at 25 °C for all of the NMR measurements. Both the ^1H and ^{13}C NMR spectra were referenced to the TMS peak at 0.0 ppm.

Quantitative $^{13}\text{C}\{^1\text{H}\}$ spectra were obtained by use of inverse-gated WALTZ-16 proton decoupling, a 30° flip angle, and a long pulse repetition time (3.635 s acquisition time, 16.4 s waiting time). The dwell time was 13.867 μs and the 90° pulse width for ^{13}C was 12 μs . A sweep width of 36057.69 Hz (-20 ppm to 220 ppm) was used. The number of data points was doubled by zero filling and exponential line broadening of 0.3 Hz was employed. After 2000 scans the spectra had signal-to-noise ratios that ranged from 1400 to 3900 for the central carbon atom of the pentaerythritol moiety. The effectiveness of these parameters for producing quantitative ^{13}C spectra was verified by comparison of the peak integral areas for the various types of carbon atoms in the spectrum for PEC5; all integral areas were within 10 % of predicted values.

Quantitative ^1H NMR spectra were obtained with a 30° flip angle and a long pulse

repetition time (a 5.45 s data acquisition time plus a 15.0 s waiting time). The dwell time was 41.6 μs . The 90° pulse width for ^1H was 15 μs . A sweep width of 12019.23 Hz (-4 ppm to 16 ppm) was used. Spectral processing was done without zero filling and with exponential line broadening of 0.3 Hz. After 128 scans the spectra had signal-to-noise ratios of approximately 1×10^5 (based on the tallest, non-solvent peak).

Karl Fischer Titration

The four base oils and the fully qualified lubricant were analyzed for water content by coulometric Karl Fischer (KF) titration. The general procedure for the Karl Fischer measurement is given in ASTM Standard Test Method E 1064-00.³⁹ A control sample was also analyzed in order to check instrument performance and repeatability. The control sample was a commercial water concentration standard (Hydranal[®]-Water Standard 1.0, distributed by Fluka Analytical⁴⁰) with a water concentration of $(999 \pm 4) \mu\text{g/g}$ according to the manufacturer. The measured water concentration in the standard was $(1000 \pm 20) \mu\text{g/g}$, consistent with expectations. The measured water content in the base oils and lubricant on a mass basis is between 200 $\mu\text{g/g}$ to 500 $\mu\text{g/g}$, as shown in Table 1. Because of the large molecular weight of the lubricants, on a molar basis these values are much higher, equating to approximately 1 mole percent.

Thermal Decomposition Apparatus and Procedures

Tubular stainless steel (316L) ampule reactors with an internal volume of about 190 μL were used to decompose the fluids of interest. The reactors were secured with a high-pressure valve, rated to 103 MPa (15000 psi), and were heated in tight-fitting slots in a thermostatted block. The block was made of 304 stainless steel, which was chosen for oxidation resistance; however, it was difficult to maintain a uniform temperature across the block due to the low thermal conductivity of this steel. In order to minimize uncertainty due to reaction temperature, rate constants were determined for distinct positions in the thermostatted

block. The temperature of the slot closest to the PID controller fluctuated the most, ± 3 K, and was typically (1 to 2) K above the set-point. The slots closest to the exterior were typically (2 to 3) K colder than the set-point, and fluctuations were ± 2 K from the mean. The reactor cell and thermostatted block for temperature control are described in more detail elsewhere.¹⁵

The cells were loaded with the appropriate amount of fluid to achieve an initial pressure of approximately 20.7 MPa (3000 psi) at a given temperature. The fluid mass was estimated with preliminary equations of state developed for PEC5 or PEC9. The appropriate mass loading of PEC7 was the average of the predicted amount of PEC5 and PEC9, and the qualified lubricant assumed contributions of 80 % PEC5 and 20 % PEC9. This proportion was chosen based on considerations of the vapor pressure, density, and average molecular weight of the fluids in the qualified lubricant. Because the vapor pressure for these lubricants is so low⁸ (5×10^{-5} Pa for PEC9 at 395 K up to 0.9 Pa for PEC5 at 413 K), the cells contained between 150 mg and 180 mg of fluid, depending on the desired reaction temperature. This quantity of fluid nearly filled the entire cell volume. The sample was transferred to the reactor with a gas-tight syringe fitted with a 26 gauge needle, and the cells were consistently filled to within 3 mg of the calculated fluid mass. Prior to heating, the cell was degassed with a single freeze-pump-thaw cycle in liquid nitrogen. Analysis by GC-FID and Karl Fisher titration of an unheated, degassed sample showed that no significant changes to the composition or the water content of the fluid occurred due to freezing and degassing. The samples were then heated in the temperature range of 500 K to 675 K with reaction times ranging from 10 min to 35 min at 675 K up to 300 h to 700 h (12 days to 30 days) at 500 K. The reactions were quenched by immersing the cell in a bath of room-temperature water at the conclusion of the test. The extent of decomposition was limited to at most a loss of 40 % of the starting material; decomposition in excess of this amount resulted in a non-linear relationship in a plot of Eq. 1, indicating that the assumption of pseudo first-order reaction kinetics is no longer valid.

After heating, the thermally decomposed liquid sample was removed from the cell in two steps. Some reaction conditions produced volatile species, which caused the final cell pressure to increase.¹⁷ In order to minimize sample loss, a short piece of bent tubing was secured to the valve and directed into a 2 mL autosampler vial to collect any expelled liquid. The remaining liquid was removed from the cell with the gas-tight syringe and diluted to a mass fraction of 5 % to 10 %. The solvents used for dilution were *n*-decane (for the lubricant mixture) or *n*-dodecane (for the pure base oils). The solvent was chosen to minimize chromatographic overlap with the decomposition products. The vial with the diluted sample was then crimp sealed with a polytetrafluoroethylene/silicone cap and kept chilled at 278 K until ready for chromatographic analysis.

The used reactors were first rinsed with acetone and sonicated for a few minutes, followed by an additional rinse and a 10 min sonication with a 50:50 mix of toluene and acetone, and one final rinse with acetone. The valves were also disassembled after each experiment to allow inspection and cleaning of the valve stem, seat, and packing (made of Teflon). The valve components were thoroughly rinsed with acetone in order to prevent contamination in subsequent experiments. Cleaned and evacuated cells and valve components were dried in an oven at 380 K for at least two hours to remove residual solvent.

The age of the ampule cell was also shown to be important for test repeatability, indicating that surface reactions are able to influence the decomposition rates of the polyol esters. This is contrary to previous decomposition studies using the ampule reactors to heat (un-oxygenated) hydrocarbon fuels.^{13,15-17} These previous experiments showed no correlation between cell age and measured decomposition rate. However, heating the pure polyol ester base oils in new, unpassivated cells resulted in decomposition products formed at a faster rate than use of an older cell heated with exactly the same conditions. Passivation with a citric acid solution⁴¹ did little to reduce the reactivity of the stainless steel reactors towards the esters. Instead, passivation of the ampule cells was accomplished by several cycles of heating the reactors loaded with the polyol esters followed by cleaning in order to build up a

sufficient surface oxide layer. A discussion of catalytic decomposition of these polyol esters is presented in the Results section.

Sample Analysis by GC-FID and GC-MS

Aliquots (1 μL) of diluted, decomposed fluids were injected into a gas chromatograph with an automatic sampler, and the separated sample detected with either a flame ionization detector (FID) for quantitative analysis or a mass spectrometer (MS) with electron ionization for chemical characterization.

The decomposed fluid was separated chromatographically on a capillary column with a non-polar stationary phase, (5%-phenyl)-methylpolysiloxane (320 μm i.d. for FID or 250 μm i.d. for MS, 0.25 μm film thickness). The injector inlet and detector were both maintained at 300 $^{\circ}\text{C}$. The injector flow into the column was split at a ratio of 40:1 for the pure base oils or 75:1 for the lubricant mixture. The flow through the column was held constant for analysis of the decomposition products from the pure fluids at 1.8 mL min^{-1} . A ramped flow setting was used for separation of the qualified lubricant: the column flow at injection was 1.8 mL min^{-1} for 1 min, followed by a 0.5 mL min^{-2} ramp to a final flow of 2.2 mL min^{-1} . The temperature program for the pure base oils started at 70 $^{\circ}\text{C}$, ramped to 250 $^{\circ}\text{C}$ (at 25 $^{\circ}\text{C min}^{-1}$), held isothermal for 0.5 min, and ramped once more at 35 $^{\circ}\text{C min}^{-1}$ to 325 $^{\circ}\text{C}$. The length of time at 325 $^{\circ}\text{C}$ depended on the molecular weight of the pure fluid. For PEC5, the required isothermal time at the upper temperature to detect all products was about 16 min; this time increased to 25 min for PEC9. The unheated qualified lubricant mixture contained more than 70 species and required a slower temperature ramp in order to achieve adequate separation. The temperature program for the mixture was 70 $^{\circ}\text{C}$ (0.5 min) to 250 $^{\circ}\text{C}$ (at 35 $^{\circ}\text{C min}^{-1}$, held 7 min), to 275 $^{\circ}\text{C}$ (at 5 $^{\circ}\text{C min}^{-1}$, held 5 min), to 325 $^{\circ}\text{C}$ (at 7.5 $^{\circ}\text{C min}^{-1}$, held 20 min). For flame ionization detection, the hydrogen flow was maintained at 30 mL min^{-1} and air flow at 200 mL min^{-1} with no make-up gas flow. Mass spectral detection was performed in scan mode and spectra were assigned with guidance from the NIST/EPA/NIH

Mass Spectral Database⁴² and previous GC-MS studies of polyol ester lubricants.^{35,36,43}

The disappearance (in terms of % of total uncalibrated area, with solvent signal removed) of the polyol esters were tracked by GC-FID to quantify the decomposition as a function of time and temperature. For the single-component base oils, this involved using only the integrated signal of a single reactant peak. For the qualified lubricant mixture, the area % of 20 pentaerythritol esters were monitored by GC-FID. These 20 species accounted for approximately 74 % of total chromatographic area (approximately 96 % of the total FID response is due to pentaerythritol esters). Tracking a set of reactants was chosen over tracking the light-weight product suite, as has been done in the past for complex fuel mixtures,^{15,17} in order to account for the formation of products that chromatographically elute in the vicinity of the reactants. No peaks in the chromatogram were deconvoluted, so it is possible that multiple species could be present under a single peak, even if the peak shape had a Gaussian distribution. The peaks chosen were shown to continuously decrease with reaction time, and ones that did not decrease were not included in this analysis, because it can be assumed that there might be new species formed that we are unable to chromatographically resolve from the reactants. In addition, pentaerythritol esters were the only species tracked for quantification of the lubricant mix, because some of the additives are consumed in order to protect the structural integrity of the polyol esters (by reacting with reactor walls and neutralizing other reactive species).³⁰

The vapor phase was also analyzed for selected samples. A description of experimental procedures^{15,44,45} and results of this analysis are included in the Supporting Information.

Accelerated Tests

Powder samples of several metals and ceramics were tested for reactivity with the pentaerythritol ester PEC9. The materials (and particle diameter provided by manufacturer or visually estimated) are included in Table 2. Approximately 1 mmol of each material (40 mg to 100 mg) was mixed with 0.4 mmol PEC9 (300 mg) and heated at 523 K for 1 h in a 2

mL borosilicate glass autosampler vial, sealed with a PTFE/silicone/aluminum cap (oxygen not removed, any vapors produced were not allowed to escape). An aliquot (10 mg) of the thermally stressed sample was diluted in *n*-decane and sampled by GC-FID to determine the fraction that decomposed. Heating in the presence of alumina resulted in the most decomposition with a loss of approximately 5 % of the base oil. Major decomposition products included a carboxylic acid, a tri-ester, and gaseous products (not sampled). Approximately 1% decomposition was observed upon heating the ester in the presence of the other materials. This was on the order of the amount observed in a control sample of only the base oil heated in the glass vial. Other key observations are also included in Table 2.

Table 2: Experimental Details for the Accelerated Tests

Material	Size* (μm)	Observations
alumina (Al_2O_3)	50–200	significant vapor phase
chromium	< 50	
copper	4–6	
copper	150	
copper (I) oxide	< 75	
iron	75	some vapors
iron	200–400	
Macor	< 100	
nickel	100	some vapors
stainless steel flake (316L)	fine, < 50	oil pale yellow

*approximate particle diameter, provided by manufacturer or estimated

Results and Discussion

The primary objective of this research was to determine the global thermal decomposition kinetics of the polyol ester lubricants. Along with these kinetic measurements, major products, and possible routes to formation are also discussed.

Decomposition Products

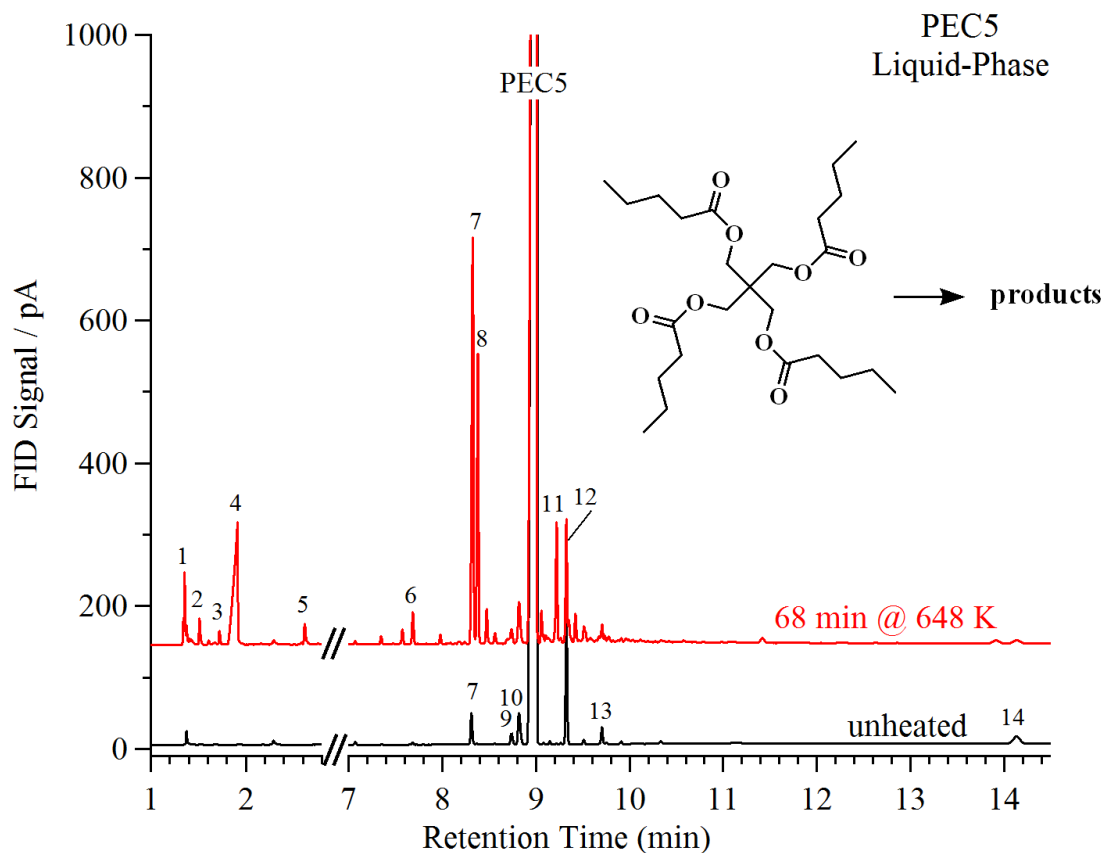


Figure 2: Gas chromatograms with flame ionization detection of unheated and thermally stressed (20 % decomposed) samples of PEC5; maximum signal height of PEC5 is approximately 4500 pA. Select products and impurities are numbered and identified in Table 3.

A gas chromatogram of unheated PEC5 (black trace) compared to a thermally stressed sample (red trace) is shown in Figure 2. The major impurities that elute from 8.7 to 14.2 min in the unheated PEC5 sample are tetraesters with different side-arm chain lengths, accounting for about 2.9 % of total area (uncalibrated FID response). As summarized in Table 1, the impurity species are polyol esters that have one acyl moiety that is not a linear pentanoate (C_5), but instead has a butanoate (C_4), branched pentanoate ($b-C_5$), heptanoate (C_7), octanoate (C_8), or nonanoate (C_9) functionality. Based on the EI-MS fragmentation patterns^{35,36} most are linear acyl groups, but we cannot rule out the possibility of additional branched species. The remaining 0.4 % of total area in the unheated sample corresponds to

Table 3: Major Products and Impurities in the Unheated and Thermally Stressed Samples of Pentaerythritol (PE) Tetrapentanoate. Peak # Corresponds to Label in Figure 2; Area % Corresponds to % of Total Uncalibrated FID Response for Unheated and Stressed Samples.

#	Identity	Unheated Area %	Stressed Area %
1	butane <i>n</i> -C ₄ H ₁₀	-	0.89
2	pentanal C ₄ H ₉ -CHO	-	0.25
3	methyl pentanoate C ₄ H ₉ -C(O)O-CH ₃	-	0.14
4	pentanoic acid C ₄ H ₉ -COOH	-	3.45
5	5-nonanone C ₄ H ₉ -CO-C ₄ H ₉	-	0.28
6	trimethylol ethane tripentanoate* (C ₄ H ₉ C(O)OCH ₂) ₃ C-CH ₃	-	0.38
7	PE tripentanoate* (C ₄ H ₉ C(O)OCH ₂) ₃ C-CH ₂ OH	0.41	5.17
8	PE acetate tripentanoate* (C ₄ H ₉ C(O)OCH ₂) ₃ C-CH ₂ OC(O)CH ₃	-	3.17
9	impurity* PE with C ₄ , C ₅ esters	0.18	0.33
10	impurity* PE with branched-C ₅ esters	0.58	0.75
	pentaerythritol tetrapentanoate (PEC5)	96.6	77.9
11	product* PE with C ₅ , C ₈ esters	-	1.44
12	impurity* PE with C ₅ , C ₇ esters	1.54	1.59
13	impurity* PE with C ₅ , C ₉ esters	0.20	0.43
14	impurity [†] unknown structure w/ C ₅ esters	0.38	0.20

* assigned by the ions: [acyl]⁺, [acyl+71]⁺ and [M-C_nH_{2n-1}COO]⁺

[†] MS fragments(rel. ab.): 687(0.1), 401(7), 371(17), 317(8), 215(10), 156(9), 85(100), 57(28)

peak #7 in Figure 2, which is identified as the polyol tri-ester, pentaerythritol tri-pentanoate, where one of the arms on the polyol is replaced by an unesterified hydroxyl group (refer to Figure S2b in the Supporting Information for the EI-MS of this species). Mass spectral assignments of the polyol esters (tetra- and tri-esters) are based on the observed acyl ions (base peak in EI-MS, *m/z* 85 for PEC5), confirmation of [acyl+71]⁺ (*m/z* 156 for PEC5), and [M-C_nH_{2n-1}COO]⁺, which is the largest stable ion (*m/z* 371 for PEC5, as shown in Figure S2a in the Supporting Information).^{36,43} For these large esters, the molecular ions, [M]⁺, are rarely observed from electron ionization.

The major products identified in the thermally decomposed sample of PEC5 are summarized in Table 3, with corresponding labels in Figure 2. The most abundant products are

the C_n carboxylic acid, where n is the chain length of the acyl moiety (C_5 , C_7 , or C_9 for the pure base fluids) and a pentaerythritol tri-ester (hydrolysis reaction product). Other, less abundant decomposition products have been identified by a combination of GC-MS⁴² and NMR (select ^1H and ^{13}C spectra are shown in Figure 3 and Figure S1 of the Supporting Information, respectively). These products include the C_{n-1} alkane, the C_n aldehyde, the methyl ester of the C_n acid, a symmetric ketone ($C_{n-1}\text{COC}_{n-1}$), and a pentaerythritol acetate tri-ester.⁴³ For PEC5, the major products are pentanoic acid (4) and pentaerythritol tripentanoate (7), with the other products/sample impurities and observed chromatographic area-% for this sample summarized in Table 3. (Also included in the Supporting Information are mass spectra for PEC7 (Figure S3), PEC9 (Figure S4), and PEB9 (Figure S5), in addition to their corresponding pentaerythritol ester products.)

The color of the base oils darkened considerably as the fluid became more thermally stressed. The colorless unstressed base fluids changed from a very pale yellow at 5 % decomposed to yellow at 15 % decomposed and then to brown at 30 % or more decomposed. It has been suggested that the formation of conjugated double bonds (for example conjugated ketones) are responsible for the color change,^{2,46} in addition to carbonaceous species (coke, etc.). Evidence in the NMR, shown in the top half of Figure 3, suggests that there are several different types of unsaturated species present in a thermally decomposed sample of PEC7, amounting to about 0.2 % of all hydrogens (^1H). Ali *et al.* assigned several polyol ester oxidation products using NMR.⁴⁶ They report that the hydrogen on a conjugated ketone has a larger chemical shift than other unsaturated species; the general assignments are indicated by dashed arrows in Figure 3. Since each molecule of PEC7 contains 60 hydrogen atoms (and if we assume each unsaturated species contains one to two hydrogens), this equates to a much larger proportion on a molar scale. We estimate that approximately 5 % of all molecular species are unsaturated in this thermally stressed sample. The ^1H NMR also shows evidence for the formation of several other aldehydes alongside the C_n aldehyde (heptanal for decomposition of PEC7), shown in the bottom half of Figure 3 (in addition to

^{13}C NMR in Figure S1b of the Supporting Information⁴⁷). The structural identity of these species was not investigated further.

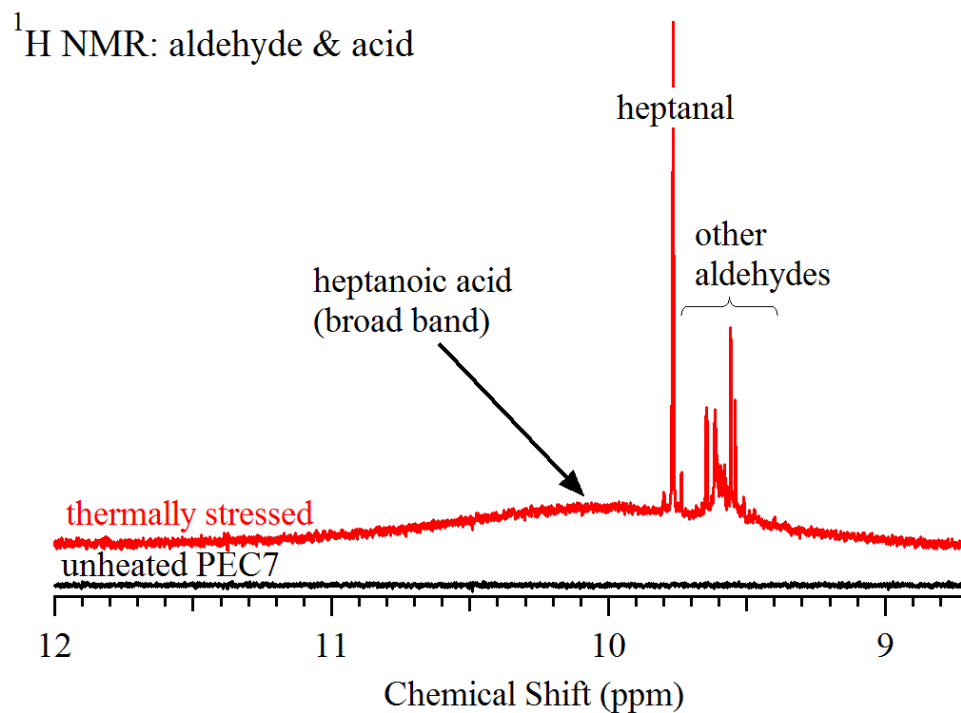
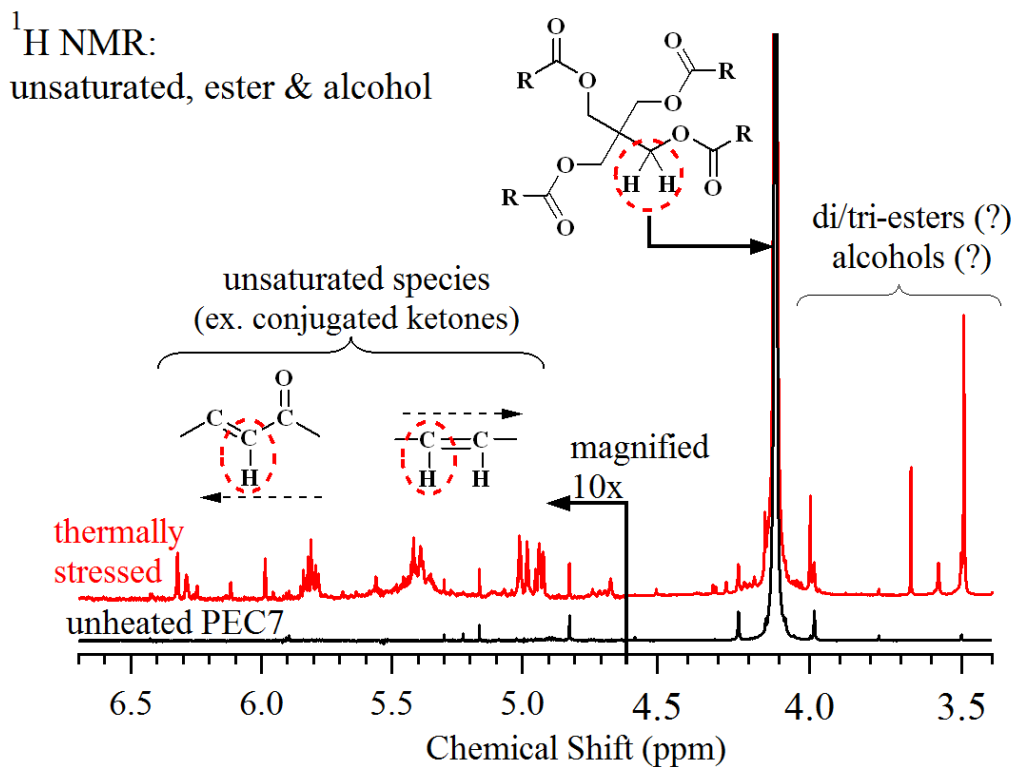


Figure 3: ^1H NMR spectra of unheated and thermally stressed (approx. 30 % decomposed) pentaerythritol tetraheptanoate (PEC7). In the upper plot the signal in the 4.6 ppm to 6.7 ppm range is magnified 10x compared to the neighboring ester protons (α -alkyl).

As described in Experimental Methods, surface reactions can influence the global decomposition kinetics of the polyol esters. This is contrary to previous decomposition studies of (un-oxygenated) hydrocarbon fuels^{13,15–17} in similar ampule reactors (316L stainless steel). Heating the pure polyol ester base oils in new, unpassivated cells resulted in the production of acids and other decomposition products at rates 1.5 to 2 times faster than use of an older cell heated with exactly the same conditions. Previous studies (summarized by Kauffman^{26,27}) have reported catalytic decomposition of the polyol esters in the presence of mild steels, cast iron, and other iron surfaces, but few studies have reported significant catalytic degradation in the presence of stainless steel. In this work, the presence of the stainless steel surface not only affected the rate of observed decomposition, but it also influenced the suite of products formed.

The origin of the symmetric ketone (species 5 in Figure 2 and Table 3) is associated with these surface reactions. The symmetric ketone is a curious species to form, because it contains two acyl groups from the polyol ester. It has been suggested that the symmetric ketone is produced by a reaction between the metal surface and a carboxylic acid and proceeds through a metal carboxylate intermediate (in the case of a steel surface, iron carboxylate).²⁹ The iron or dissolved iron species form a bond with the carbonyl oxygen on the polyol ester that reduce its barrier to decomposition. Several prior studies^{28,29} suggest that the formation of iron carboxylates (summarized in reviews by Kauffman^{26,27}) are often responsible for the premature thermal degradation of polyol esters.

Catalytic decomposition has been reported to be most pronounced in closed systems (analogous to the ampule reactors used here), where volatile species such as carboxylic acids and dissolved water remain in solution. The presence of dissolved water has been implicated in the decomposition mechanism of polyol esters, and may be an important initiating reagent,^{25,26} promoting reaction and reducing the thermal stability. As summarized in Table 1, there is between 240 $\mu\text{g g}^{-1}$ to 500 $\mu\text{g g}^{-1}$ of water in the various fluids. Even a minor hydrolysis contribution to form a carboxylic acid and an alcohol-terminated tri-ester could

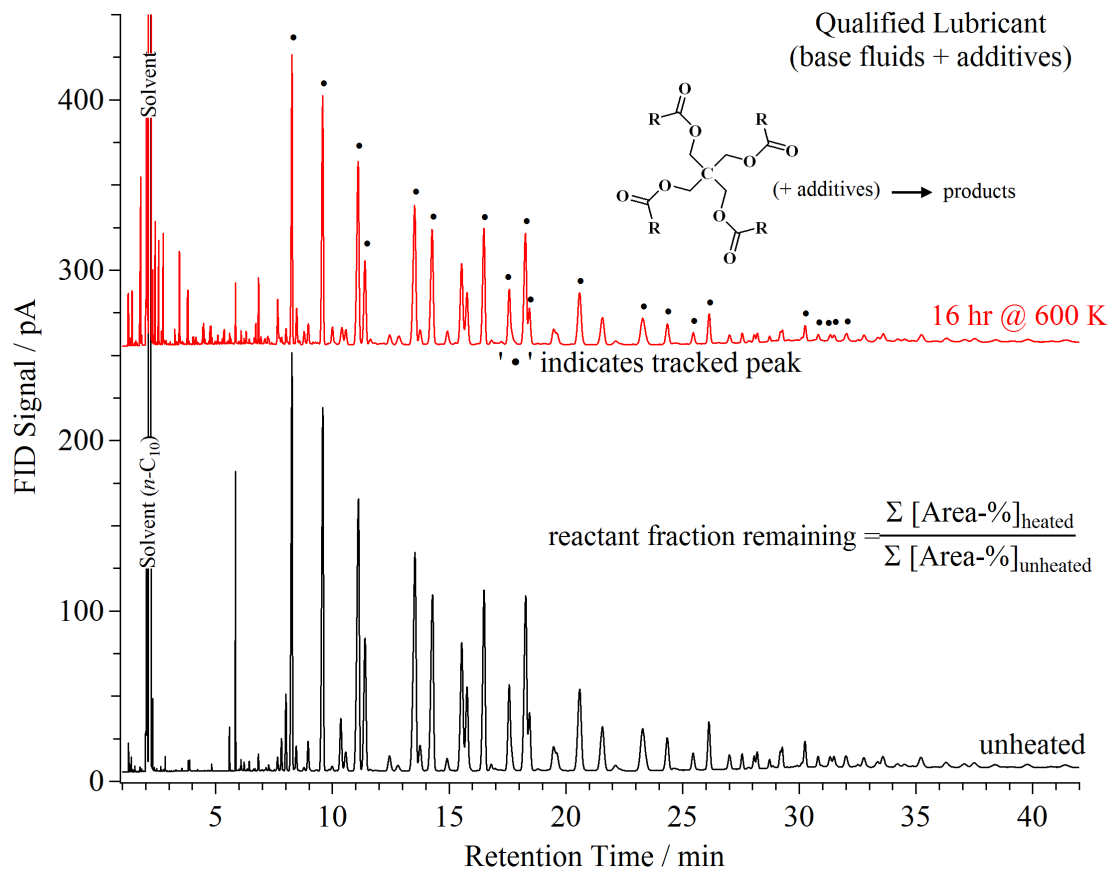


Figure 4: Gas chromatogram with flame ionization detection of unheated and thermally decomposed samples of the qualified lubricant; peaks with a ‘•’ above them were used to determine the global decomposition kinetics.

initiate decomposition in the vicinity of certain surfaces. From here, the surface catalyst in the presence of the carboxylic acid reacts to form the carboxylate and regenerates the water molecule consumed in the original hydrolysis reaction. The presence of the hydroxyl-terminated tri-ester (species 7 in Table 3) in solution may also decrease the ester’s thermal stability by increasing the quantity of water in the product suite. Dehydration of the tri-ester, in the presence of a metal catalyst, can produce water and unsaturated esters.²⁶ Essentially these previous studies demonstrate that the thermal stability is only minimally influenced by the bond strengths of the molecule itself, but instead is much more dependent upon the purity of the starting material and the type of surfaces the ester is exposed to.

Upon historical observation of catalytic degradation of the polyol esters in the presence

of certain metal surfaces, additives were developed to inhibit catalysis. A common additive for metal passivation is tricresyl phosphate (TCP). Early tests by Cottingham *et al.* showed that TCP improved the thermal stability of polyol esters by passivating the catalytic steel surfaces.²⁵ The organophosphate will either form a layer of adsorbed molecules on the surface, or with heated surfaces TCP will fragment.³⁰ Studies have shown that TCP does little to prevent decomposition and improve thermal stability without a metal surface present. Other important additives for polyol ester stability include various aliphatic amines to neutralize the TCP-derived acids and serve as antioxidants.

Similar to the decomposition of the pure base oils, the major products from thermal decomposition of the qualified lubricant were carboxylic acids. Gas chromatograms comparing unheated and thermally stressed samples of the lubricant are shown in Figure 4. Polyol ester base oils make up approximately 96 % (by mass) of the lubricant mixture; these species start to elute at about 8 min in Figure 4. The additives, which are the remaining 4 % (or less) of the mixture, elute between 5 to 8 min, just prior to the smallest polyol esters. The species labeled with a ‘●’ above them in Figure 4 were used to determine the global decomposition kinetics, which will be discussed in the following section. Decane was chosen as the solvent because it did not chromatographically interfere with the major products.

Symmetric ketones were not observed as decomposition products from the qualified lubricant, supporting the theory²⁶ that these species are the result of surface-catalyzed reactions. Accordingly, these reactions are eliminated with the addition of TCP. Unlike the experiments with the pure base oils, the age of the cell also did little to effect the amount of observed decomposition of the lubricant under any operating conditions. There were also less volatiles produced during the decomposition of the lubricant; however, the color change was more pronounced for the same reaction conditions, but likely due to the decomposition of the additives (TCP and amines) in addition to (conjugated) unsaturation in the polyol ester decomposition products.

Thermal Decomposition Kinetics

The pseudo-first-order decomposition kinetics were measured by following the extent of decomposition of the main reactant peak, in the case of the pure base oils (PEC5, PEC7, PEC9, PEB8), or several base oil peaks, as indicated in Figure 4, for the lubricant. Four nominal temperatures were tested in the 600 K to 675 K range (600 K, 625 K, 650 K, and 675 K) for all five fluids. Thermal decomposition experiments for PEC5 and the lubricant were extended to lower temperatures (500 K and 525 K), which required reaction times on the order of days to weeks in order to report an observable level of decomposition. At each temperature, a minimum of three different reaction times were tested (except PEC5 at 496 K which had only two reaction times). The natural logarithm of the remaining unreacted fraction (described in Eq. (1)) was plotted against reaction time, as illustrated in Figure 5, to obtain pseudo-first-order rate constants, k' .

The experimental data in the 600 K to 675 K temperature regime is well-represented by a pseudo-first-order expression (linear regression), as shown in the right half of Figure 5. The experimental data at lower temperatures (500 K to 525 K) did not follow this linear trend as precisely, as the left half of Figure 5 indicates. Duplicate reaction time experiments for PEC5 at 520 K were performed (solid circles in left-half of Figure 5), with similar trends observed. The shape of the curves at the lower temperatures indicate that the decomposition reaction is not adequately modeled as first order. One reason for this could be that the amount of decomposition observed was very small (less than 4 % of starting material has decomposed). Longer reaction times are needed in this temperature regime to reduce measurement uncertainty.

Summaries of the pseudo-first-order rate constants and estimated lifetimes (half-life and time to loss of 1 % of starting material) are tabulated in Tables 4 through 7 for the base oils and Table 8 for the qualified lubricant. The rate constants are also summarized in an Arrhenius plot in Figure 6. The reported uncertainties for the rate constants (k') and the activation energies (E_a , in Table 9) were determined from linear regression statistics,

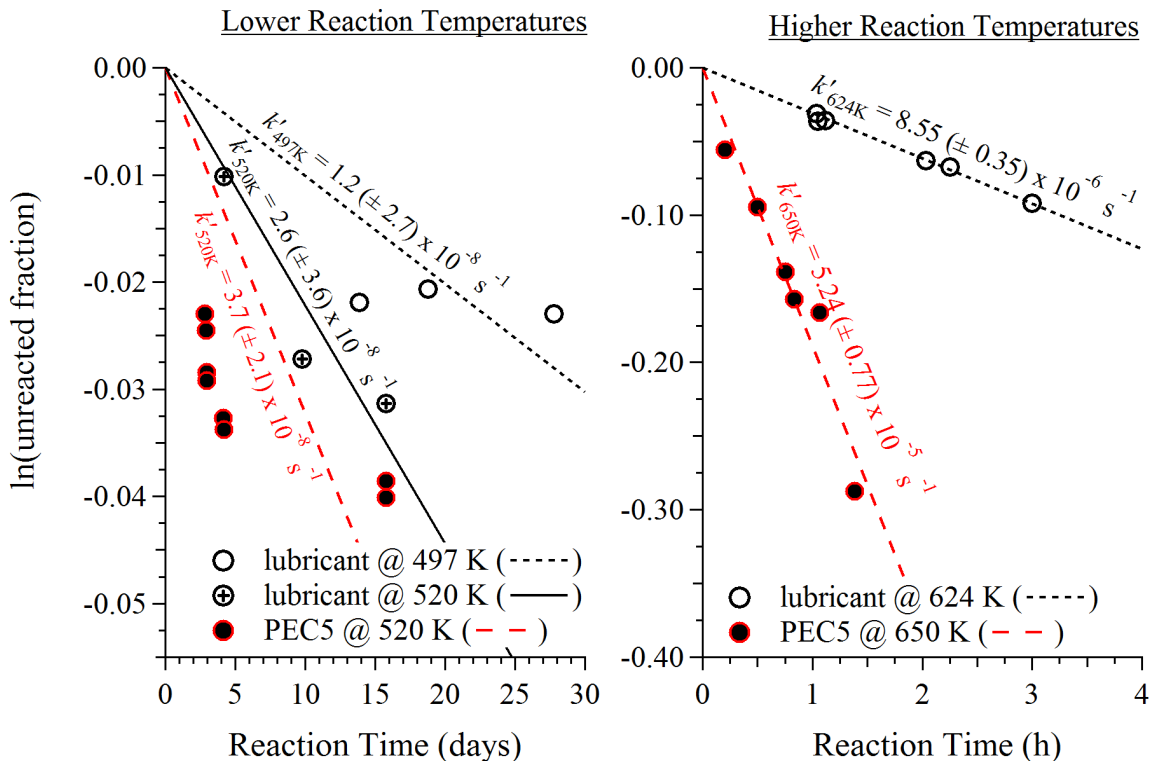


Figure 5: Select data for determining the decomposition rate constants for PEC5 and the qualified lubricant. The lower temperatures required long reaction times and observed decomposition was still minimal; note that the two plots do not have the same y -axis range. Expanded uncertainties for the rate constants (k') are based on the linear regression fit.

assuming a 95 % confidence interval (a coverage factor of 2) for the fit coefficients.

Only two other prior thermal decomposition studies of polyol esters that report extent of decomposition as a function of reaction time have been identified. Yutina *et al.* reported the degree of conversion for pentaerythritol tetrahexanoate (PEC6) at 613 K (340 °C).⁴⁸ Klaus *et al.* also reported the thermal characteristics of several organic esters at 588 K (315 °C), including a mixture pentaerythritol tetrabutanoate/tetrahexanoate and trimethylol propane (TMP) triheptanoate, a tri polyol esterified with heptanoic acid.²⁸ They did not report data for the mixture of C₄/C₆ polyol tetraesters, but stated that measurements on the pentaerythritol moieties were similar to the TMP ester. From these two studies we have extracted pseudo-first-order rate constants to represent their data and have included them alongside our results in Figure 6.

Table 4: Thermal Decomposition Kinetic Data for Pentaerythritol Tetrapentanoate (PEC5)

T (K)	k' (s^{-1})	$t_{0.01}$ (min)	$t_{0.5}$ (h)
496	$1.60 (\pm 0.69) \times 10^{-8}$	10 500 (7.3 d)	12 000 (500 d)
520	$3.74 (\pm 2.1) \times 10^{-8}$	4 480 (3.1 d)	5 150 (215 d)
596	$2.42 (\pm 0.67) \times 10^{-6}$	69	80
625	$1.16 (\pm 0.33) \times 10^{-5}$	14	17
650	$5.24 (\pm 0.77) \times 10^{-5}$	3.2	3.7
675	$2.26 (\pm 0.66) \times 10^{-4}$	0.8	0.9

Table 5: Thermal Decomposition Kinetic Data for Pentaerythritol Tetraheptanoate (PEC7)

T (K)	k' (s^{-1})	$t_{0.01}$ (min)	$t_{0.5}$ (h)
595	$2.46 (\pm 0.64) \times 10^{-6}$	68	78
625	$1.09 (\pm 0.13) \times 10^{-5}$	15	18
650	$5.17 (\pm 0.41) \times 10^{-5}$	3.2	3.7
675	$2.00 (\pm 0.34) \times 10^{-4}$	0.8	1.0

In general, all pure linear polyol esters, regardless of size, exhibit very similar decomposition behavior within the limits of uncertainty of the measurement. Oxidation studies have shown that reactivity typically increases with increasing chain length,² primarily because the larger chains contain more available protons for intrachain abstraction. Based on results reported here, molecular size does not appear to be a relevant parameter for reactions that take place in the absence of oxygen. Instead, the extent of complete esterification of the starting material is a more important parameter for thermal stability. The branched base oil (pentaerythritol tetra-3,5,5-trimethylhexanoate, PEB9), which was manufactured 15 years ago, is slightly more reactive than the newer fluids, as shown in the inset of Figure 6. This base oil also contains the highest percentage of incomplete esterification (at least 0.7 %), which is a factor of two to seven more than the newer fluids. With the addition of the additives to reduce surface effects, the qualified lubricant has a lifetime (when heating in the absence of oxygen) that is on average 1.7 times that of the pure base oils that contain no additives.

The decomposition rate constants measured by Klaus *et al.*²⁸ and Yutina *et al.*⁴⁸ are

Table 6: Thermal Decomposition Kinetic Data for Pentaerythritol Tetranonanoate (PEC9)

T (K)	k' (s^{-1})	$t_{0.01}$ (min)	$t_{0.5}$ (h)
595	$1.91 (\pm 0.62) \times 10^{-6}$	88	101
625	$1.16 (\pm 0.33) \times 10^{-5}$	14	17
650	$5.25 (\pm 0.26) \times 10^{-5}$	3.2	3.7
675	$2.45 (\pm 0.34) \times 10^{-4}$	0.7	0.8

Table 7: Thermal Decomposition Kinetic Data for Pentaerythritol Tetra-3,5,5-trimethylhexanoate (PEB9)

T (K)	k' (s^{-1})	$t_{0.01}$ (min)	$t_{0.5}$ (h)
595	$2.15 (\pm 0.33) \times 10^{-6}$	78	90
625	$1.76 (\pm 0.81) \times 10^{-5}$	10	11
652	$8.48 (\pm 1.3) \times 10^{-5}$	2.0	2.3
678	$2.56 (\pm 0.27) \times 10^{-4}$	0.7	0.8

about twice that of the linear polyol esters reported here. The trend of the rate constants for the branched polyol ester (PEB9, solid red circles in Figure 6) more closely resembles the rate constants from these previous measurements. One possible reason for the discrepancy could be that the purity of their samples may have been less than those reported here, which provided more initiating reagents necessary for decomposition.

The extrapolated Arrhenius parameters for the five test fluids are reported in Table 9. The parameters for PEC5 and the qualified lubricant were determined over the temperature range 500 K to 675 K. Due to the large measurement uncertainty for the lower temperature measurements, as indicated in Figure 6 and previously discussed, the Arrhenius fit for these two fluids was weighted based on the measurement uncertainty (reciprocal of the standard deviation). The large uncertainty in the lower temperature measurements (500 K and 525 K) could have systematic contributions that we are unable to quantify; therefore we assume these measurements should contribute less to the Arrhenius fit than the higher temperature measurements. The Arrhenius fit parameters for remaining base oils (PEC7, PEC9, and PEB9) are not based on a weighted fit; we assume that the contributions to the uncertainty

Table 8: Thermal Decomposition Kinetic Data for the Fully Qualified Lubricant

T (K)	k' (s^{-1})	$t_{0.01}$ (min)	$t_{0.5}$ (h)
497	$1.17 (\pm 2.7) \times 10^{-8}$	14 350 (10 d)	16 500 (685 d)
520	$2.57 (\pm 3.6) \times 10^{-8}$	6 500 (4.5 d)	7 500 (313 d)
596	$1.49 (\pm 1.06) \times 10^{-6}$	158	182
625	$8.55 (\pm 0.35) \times 10^{-6}$	20	23
650	$3.71 (\pm 0.35) \times 10^{-5}$	4.5	5.2
675	$1.34 (\pm 0.26) \times 10^{-4}$	1.3	1.4

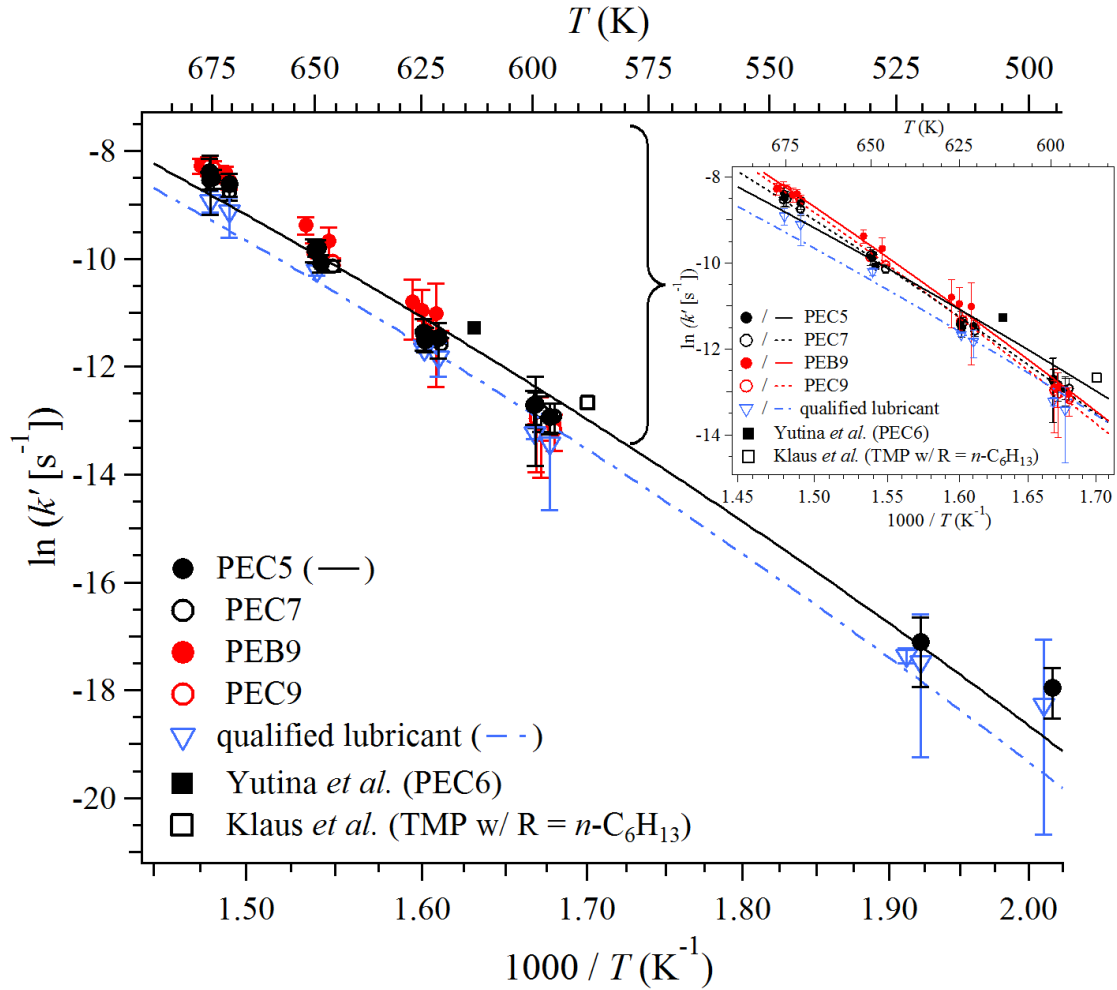


Figure 6: Arrhenius plot of the first-order rate constants, k' ; uncertainty limits are derived from the expanded uncertainty (coverage factor of 2) of the linear regression fit. The square symbols (\blacksquare, \square) are rates from previous polyol ester thermal decomposition studies (TMP = trimethylol propane).^{28,48} Inset shows expanded plot of 600 K to 675 K, with all Arrhenius fits included.

Table 9: Arrhenius Parameters for the Pure Base Oils and Lubricant

Fluid	T (K)	A (s^{-1})	E_a ($kJ\ mol^{-1}$)
PEC5	500–675	2.28×10^8	158 ± 10
PEC7	600–675	5.64×10^{10}	187 ± 6
PEC9	600–675	1.41×10^{12}	204 ± 5
PEB9	600–675	5.03×10^{11}	197 ± 11
lubricant	500–675	2.62×10^8	161 ± 7

for these measurements is uniform across the temperature range and should not be subject to a weighted fit. The evidence indicates that the largest contributors to the uncertainty in all the thermal stability measurements are the sample purity, condition of the reactors, and chromatographic separation. Influences due to fluctuating reaction temperatures are minor in comparison.

Conclusions

We have measured the global thermal decomposition kinetics of four pentaerythritol tetraester base oils and one qualified (MIL-PRF-23699) polyol ester lubricant. Pseudo-first-order rate constants and Arrhenius parameters were measured from 500 K to 675 K with an initial reaction pressure of approximately 20.7 MPa. Although these fluids are known for their thermal stability, thermal decomposition rate constants that span over this temperature range have not been previously reported. In general, the results of these experiments show that, for the purpose of performing thermophysical property measurements on these fluids, the fluid temperature can be maintained at 500 K for several days with less than 1 % sample decomposition. Property measurement conditions requiring a temperature in excess of 600 K should be completed within about one to two hours in order to avoid more than 1 % decomposition of the fluid.

The results of the Arrhenius fit of PEC5 and the qualified lubricant over the temperature range 500 K to 675 K compared to the base oils over a smaller temperature range (600 K to

675 K) indicate a need for additional measurements to reduce the uncertainty of the lower temperature measurements. Longer reaction times at the lower temperatures, in addition to measurements at intermediate temperatures, would help to bridge the gap and improve the fit. It is possible that decomposition may be initiated by a different mechanism at the lower temperatures, which makes applying a pseudo first-order kinetic approximation inappropriate; future measurements to address these issues would also be of value.

Finally, new (unpassivated) stainless steel ampule reactors (in addition to an alumina surface) also demonstrated catalytic behavior towards the pure polyol ester base oils, indicating that the condition of the wetted surfaces was important for accurate measurements. This behavior was absent in the lubricant which contained additives to prevent decomposition due to surface chemistry or possible solution impurities.

Acknowledgement

The authors thank James McDonnell and Dawn Schmidt at the Naval Air Systems Command (NAVAIR) for supplying the lubricant and base fluids, in addition to helpful discussions. K.N.U. gratefully acknowledges a National Academy of Sciences/National Research Council postdoctoral fellowship. R.V.G. acknowledges support from the Professional Research Experience Program (PREP) for research performed at NIST in Boulder.

Supporting Information Available

Supporting Information: ^{13}C NMR spectra of quarternary and carbonyl carbon regions (Figure S1); mass spectra of base oils and major pentaerythritol products (Figures S2 through S5); description and qualitative analysis of vapor-phase products (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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