

THERMAL DECOMPOSITION OF RP-1, RP-2, AND MIXTURES OF RP-2 WITH STABILIZING ADDITIVES

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ABSTRACT

The thermal decomposition of RP-1, RP-2, and mixtures of RP-2 with three different additives has been investigated. The mixtures with RP-2 contained 5 % 1,2,3,4-tetrahydronaphthalene (tetalin), 5 % 1,2,3,4-tetrahydroquinoline (THQ), or 256 mg/L of the additive used to make JP-8+100. Decomposition reactions were performed in stainless steel ampoule reactors at temperatures from 375 °C to 450 °C (648 K to 723 K). All of the reactions were run with an approximate initial pressure of 5000 psi (34.5 MPa). After each reaction the thermally stressed liquid phase was analyzed by gas chromatography. For RP-1 and RP-2, the increase in a suite of light decomposition products was used to derive global, pseudo-first-order rate constants that approximate the overall rate of decomposition. For RP-2, decomposition rate constants ranged from $1.33 \times 10^{-5} \text{ s}^{-1}$ at 375 °C to $5.47 \times 10^{-4} \text{ s}^{-1}$ at 450 °C. The rate constants for RP-1 decomposition were not significantly different. The addition of THQ and tetralin had a significant effect on the decomposition of RP-2. Compared with neat RP-2, the addition of 5 % THQ slowed the decomposition by an order of magnitude, while the addition of 5 % tetralin slowed the decomposition by approximately 50 %.

INTRODUCTION

A large-scale project¹⁻⁸ involving the thermophysical properties of kerosene-based rocket propellants is in progress at the National Institute of Standards and Technology (NIST) as well as other facilities. This work is meant to enhance design and operational specifications for these fluids and facilitate new applications.^{9,10} The thermophysical properties that are being measured include equilibrium properties (such as the fluid density, vapor pressure, volatility, speed of sound and heat capacity) and transport properties (such as viscosity and thermal conductivity). Some of these property data for RP-1 and RP-2 have already been reported.^{1-3,5} The ultimate goal of the thermophysical property measurements at NIST is the development of equations of state to describe the properties.^{2,11-13}

Understanding the thermal stability of RP-1 and RP-2 is important for a variety of reasons.^{4,14-19} One important motivation for our work was to ensure the quality of thermophysical property data that were collected at higher temperatures. The formation of both light and heavy decomposition products is a concern because either can cause significant changes in the properties of the fluid. Additionally, the formation of solid deposits inside instruments can cause systematic errors in the data that are difficult to detect. However, if one understands the kinetics

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of decomposition, it is possible to avoid such problems by setting residence-time limits for high-temperature measurements.²

In addition to impacting data quality, the formation of decomposition products can damage the instruments themselves. Solid deposits (which plug capillaries, coat sensors, change internal volumes, etc.) can be difficult to remove. The formation of light decomposition products can result in a catastrophic increase in pressure in a closed system. Again, the key to avoiding such problems is to understand the kinetics of decomposition.

When planning high-temperature property measurements, it is useful to know the “global” Arrhenius parameters for decomposition, which can be used to predict decomposition rates at any given temperature.^{4,20-25} The Arrhenius parameters are determined from a plot of the rate constants for decomposition as a function of the temperature. In the case of complex mixtures like RP-1 and RP-2, rate constants for decomposition (and the Arrhenius parameters determined from them) will necessarily be approximate because they describe a complex series of reactions.^{4,20} Nevertheless, we have found that such an approach still yields information that is useful for determining residence-time constraints on measurements conducted at high temperature.

The thermal stability of kerosene-based rocket propellants is also a key design parameter for specifying their performance.^{26,27} The rocket propellant serves the dual roles of fuel and coolant in modern rocket engines. Prior to combustion, the rocket propellant circulates through channels in the wall of the thrust chamber. Thus, the fuel carries heat away from the wall and maintains a safe wall temperature. This process, commonly referred to as regenerative cooling, exposes the fuel to high temperatures. For this reason, the thermal stability of the kerosene-based rocket propellant RP-1 has been studied extensively.^{14,15,17-19,26,27} The thermal stability of a relatively new rocket propellant, RP-2, has been the subject of fewer studies.^{15,17,28,29} The specification for RP-2, along with an updated specification for RP-1, was published in 2005 as MTL-DTL-25576D. The primary differences between the specifications for RP-1 and RP-2 are that the allowed sulfur content is much lower in RP-2 (0.1 mg/kg, compared to 30 mg/kg in RP-1), the allowed olefin concentration is lower in RP-2 (1 vol %, compared to 2 vol % for RP-1), and the use of the red dye is not allowed in RP-2. All three of these differences were intended to increase the thermal stability of RP-2 and facilitate reusable rocket motors.

A potential approach for further improvements in the thermal stability of RP-2 is to use stabilizing additives. The use of additives has a long history with kerosene-based jet fuels.^{26,30} Much of the work on jet fuels has focused on additives that are “hydrogen donors”, such as 1,2,3,4-tetrahydroquinoline (THQ),³¹⁻³³ 1,2,3,4-tetrahydronaphthalene (tetalin),^{31,33-38} decahydronaphthalene (decalin),^{36,38} and benzyl alcohol.^{31,39-41} In related work, a major research effort initiated by the U.S. Air Force culminated in the formulation the stabilizing additive package used to make JP-8+100 (herein referred to as the “+100 additive”). The +100 additive contains three components: an antioxidant (hydrogen donor), a metal deactivator, and a dispersant (surfactant).²⁶ The use of such stabilizing additives has been suggested²⁷ for rocket propellants, but little work has been done.^{17,26}

This paper constitutes a review of three recent studies of the thermal stability of kerosene-based rocket propellants.^{4,28,29} Herein we summarize the results for five samples: RP-1, RP-2, RP-2 with 5 % THQ, RP-2 with 5 % tetralin, and RP-2 with 256 mg/L of the +100 additive (hereafter the mixtures are referred to as, RP-2+THQ, RP-2+tetralin, and RP-2+100). Aliquots of each sample were thermally stressed in sealed stainless steel reactors at temperatures from 375 °C to 450 °C (648 K to 723 K). At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography. For RP-1 and RP-2, these data were used to derive pseudo-first-order rate constants that approximate the overall decomposition rate of the fuel. The rate constants were then used to estimate Arrhenius parameters for each fuel. The effectiveness of each stabilizer was determined by comparing the amount of decomposition in the mixture to the amount of decomposition in neat RP-2.

EXPERIMENTAL

CHEMICALS

Reagent-grade acetone, toluene and dodecane were used as solvents in this work. They were obtained from commercial sources and used as received. All had stated purities of no less than 99 %, which is consistent with our own routine analyses of such solvents by gas chromatography. The THQ (98 % purity) and tetralin (99.5 % purity) were also obtained from commercial sources and used as received. The +100 additive and the RP-1 were obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Wright Patterson Air Force Base). The RP-1, which was from a batch with the identification number POSF 4572, was pink because it contained the red dye azobenzene-4-azo-2-naphthol. The RP-2 was also obtained from the AFRL (Edwards Air Force Base). It did not contain the dye, so it was clear and colorless.

APPARATUS

The apparatus used for the decomposition reactions is shown in Figure 1. Two thermostatted blocks of 304 stainless steel (AISI designation) were used to control the reaction temperature. Each block was supported on carbon rods in the center of an insulated box. A proportional-integral-derivative controller used feedback from a platinum resistance thermometer to maintain the temperature within 1 °C of the set value. As many as six stainless steel ampoule reactors could be placed into tight-fitting holes in each of the thermostatted blocks. Each reactor consisted of a tubular cell with a high-pressure valve. Each cell was made from a 5.6 cm length of ultrahigh-pressure 316L stainless steel tubing that was sealed on one end with a 316L stainless steel plug welded by a clean tungsten-inert-gas (TIG) process. The other end of each cell was connected to a valve with a 3.5 cm length of narrow-diameter 316 stainless steel tubing that was TIG-welded to the larger diameter tube. The valves were appropriate for high temperature in that the seats were stainless steel and the packings were flexible graphite. Each cell and valve was capable of withstanding a pressure of at least 100 MPa (15000 psi) at the temperatures used. The internal volume of each cell was determined gravimetrically from the mass of toluene required to fill it (approximately 0.11 mL).

It is possible that the surface properties of the reactors change with age and use. This could potentially change the amount of surface-catalyzed decomposition and shift the observed rate constants for decomposition. Our experimental design accounts for such a possibility in the following way. At any one time we have a set of 15 reactors that are used for decomposition studies. Individual reactors occasionally fail (by developing a leak, etc.), and are replaced by new reactors. Consequently, the reactors that we used for this decomposition study were of varying ages. Additionally, the different temperatures and reaction times were done in a randomized order. Consequently, any effects of reactor aging should already be observable as scatter in the data (and, therefore, included in the uncertainty estimates for the rate constants). Since scatter in the data is small, we conclude that surface aging in the reactors is not very important in this system. This conclusion also suggests that surface catalysis is not very important for these fluids.

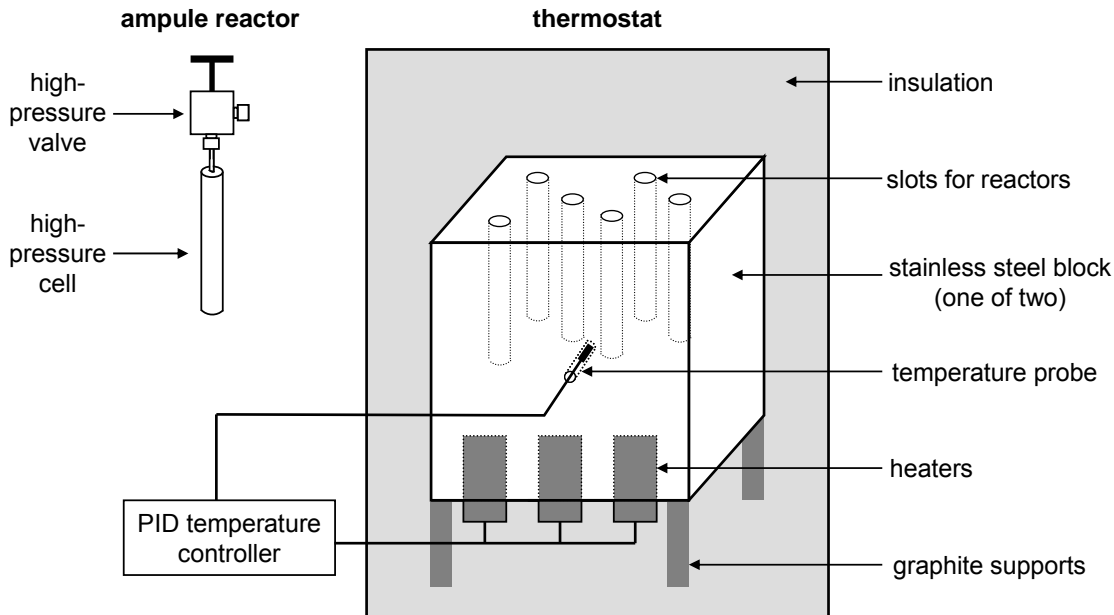


Figure 1. Apparatus Used to Thermally Stress RP-1 and RP-2.

DECOMPOSITION REACTIONS

The procedure used to fill the reactors was designed to achieve an initial target pressure of 34.5 MPa (5000 psi) for all decomposition reactions.⁴ This is important because it mimics the high-pressure conditions during some physical property measurements, and it helps ensure that differences in observed decomposition rates are due only to differences in temperature (and not to differences in pressure). With an equation of state for n-dodecane, a computer program calculated the mass of n-dodecane needed to achieve a pressure of 34.5 MPa at a given temperature and cell volume.⁴² We then assumed that the same mass of each fuel would yield a pressure close to our target pressure. This is a reasonable assumption because, although the rocket propellants are complex mixtures, models derived from the properties of n-dodecane have been used successfully to approximate the physical properties of kerosene-based fuels.^{43,44} The calculated mass of rocket propellant was added to the cell (sample masses were typically on the order of 0.06 g and varied depending on the experimental temperature and measured cell volume). The valve was then affixed to the cell and closed. Cells were then chilled to 77 K in liquid nitrogen, and subsequently the head space was evacuated to 10 Pa through the valve to remove air from the cell. The valve was then re-closed, and the cell was warmed to room temperature. The single freeze-pump-thaw cycle should remove the air from the vapor space in the cell without removing dissolved air from the fuel itself. This mimics the conditions under which the fuels are actually used (i.e., they contain dissolved air). The other advantage of doing only one freeze-pump-thaw cycle is that it limits the chances of removing more volatile components from the fuel. More rigorous degassing procedures, such as bubbling inert gas through the fuel, can change the fuel composition by removing some of the more volatile components. It is also worth mentioning that the autoxidation reactions caused by dissolved oxygen are thought to be relatively unimportant for hydrocarbon fuel decomposition above 250–300 °C.⁴⁵

The loaded reactors were then inserted into the thermostatted stainless steel block, which was maintained at the desired reaction temperature. Fluid reflux inside the cells was minimized by putting the entire reactor inside the insulated box (although only the cell tubing was inserted into the thermostatted block). The reactors were maintained at the reaction temperature for a specified period ranging from 10 min to 24 h. In order to minimize the time required for temperature equilibration, only one reactor at a time was placed in the thermostatted block if the

reaction time was less than 30 min. With this procedure, we estimate that the effective thermal equilibration (warm-up) time is approximately 2 min for a reaction temperature of 450 °C.⁴⁶ After decomposition, the reactors were removed from the thermostatted block and immediately cooled in room-temperature water. The thermally stressed fuel was then recovered and analyzed as described in the next section.

After each run, the cells and valves were rinsed extensively with a mixture of acetone and toluene. The cells were also sonicated for five minutes (while filled with the solvent mixture) between rinsings in order to remove any solid deposits that may have formed on their walls. Cleaned cells and valves were heated to 150 °C for at least 1 h to remove residual solvent.

Blank experiments were occasionally performed to check the effectiveness of this protocol for cleaning the cells. For these blank experiments, a cell was loaded with fuel as described above, but the cell was not heated above room temperature. After a day, the fuel in the cell was removed and analyzed by gas chromatography (as described in the following section). The success of the cleaning procedure was confirmed by the visual absence of color or solids in the unheated fuel, and by the absence of decomposition products in the resulting gas chromatogram.

ANALYSIS OF LIQUID-PHASE DECOMPOSITION PRODUCTS BY GAS CHROMATOGRAPHY

The production of light decomposition products caused the pressure in the reactors to increase during the decomposition reactions. After decomposition, the reactors contained a pressurized mixture of vapor and liquid, even at room temperature. Liquid-phase decomposition products in the thermally stressed fuel were used to monitor the extent of decomposition. Therefore, a sampling procedure was designed to minimize loss of the liquid sample when the reactors were opened. Specifically, a short length of stainless steel tubing was connected to the valve outlet on the reactor. The end of this tubing was placed inside a chilled (7 °C) glass vial, and the valve was slowly opened. Often, some of the reacted fuel was expelled into the vial, especially for the more highly thermally stressed samples. The valve was then removed from the reactor and any liquid remaining in the cell was transferred to the glass vial with a needle and syringe. The vial was sealed with a silicone septum closure, and the mass of liquid sample was quickly determined (with an uncertainty of 0.0001 g). The liquid sample was then immediately diluted with a known amount of n-dodecane and refrigerated until the analysis was performed. The resulting n-dodecane solution was typically 5 % reacted fuel (mass/mass). The purpose of this procedure was to prepare the samples for GC analysis and to minimize evaporative losses from the samples. One of the reasons for using n-dodecane is that it does not interfere with the GC analysis of early eluting decomposition products, yet it serves as an effective storage medium for the sample.

Aliquots from crimp-sealed vials of each sample were injected into a gas chromatograph equipped with an automatic sampler and a flame ionization detector (FID). Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was maintained at 300 °C, and samples were separated on a 30 m capillary column coated with a 0.1 µm film of (5 %-phenyl)-methylpolysiloxane.⁴⁷ The temperature program consisted of an initial isothermal separation at 80 °C for 4 min, followed by a 20 °C/min gradient to 275 °C. This final temperature was held constant for 2 min. The FID was maintained at 275 °C. Chromatograms of unheated fuel exhibited only very small peaks with retention times of less than 3.2 min; however, following thermal stress, a suite of decomposition products was observed to elute earlier than 3.2 min. The total peak area (arbitrary units) of this suite of decomposition products was used for the kinetic analysis of decomposition. Peak areas were corrected for dilution in n-dodecane by multiplying by the dilution factor. Peak areas were also corrected for drifts in detector response by analyzing an aliquot of a stock solution (pentane and hexane in n-dodecane) along with each set of decomposition samples. The simple use of peak area for the kinetic analysis is possible only because of the types of compounds being analyzed and the use of a FID. For hydrocarbons, the relative sensitivity of the detector (based on moles of carbon) varies by only a few percent.⁴⁸

Consequently, calibrating the detector for each individual compound is not expected to significantly change the derived rate constants or the comparisons of additive effectiveness.

RESULTS AND DISCUSSION

Aliquots of RP-1, RP-2, RP-2+THQ, RP-2+tetralin, and RP-2+100 were thermally stressed in stainless steel ampoule reactors at an initial pressure of 34.5 MPa (5000 psi). For RP-2+100, reaction temperatures of 375 °C and 425 °C were used. For the other four samples, reaction temperatures of 375 °C, 400 °C, 425 °C, and 450 °C were used. This temperature range was chosen, in part, because it allowed for reaction times of a convenient length. At 375 °C, the reaction is relatively slow, so reaction times ranged from 6 to 24 h. At 450 °C, the reaction is much faster, so reaction times ranged from 10 to 40 min.

The thermally stressed liquid phase of every decomposition reaction was analyzed by a gas chromatograph equipped with a flame ionization detector (GC-FID). Figure 2 shows the early part of the chromatograms obtained for both thermally stressed and unstressed RP-1 and RP-2. For each of these fuels, an emergent suite of light, liquid-phase decomposition products develops in the thermally stressed fuel (circled in Figure 2). These emergent product suites were remarkably similar for RP-1 and RP-2.

The thermal decomposition of fuels like RP-1 and RP-2 is very complex. There are a large number of compounds in the fuel, each compound may decompose by more than one reaction pathway, the decomposition reactions may yield more than one product, and the initial decomposition products may further decompose to other products. Because of this complexity, a simplifying assumption is necessary in order to gain insight into the overall thermal stability of such a fuel. In this work, we assumed that the emergent suite of light decomposition products is representative of all the decomposition products.

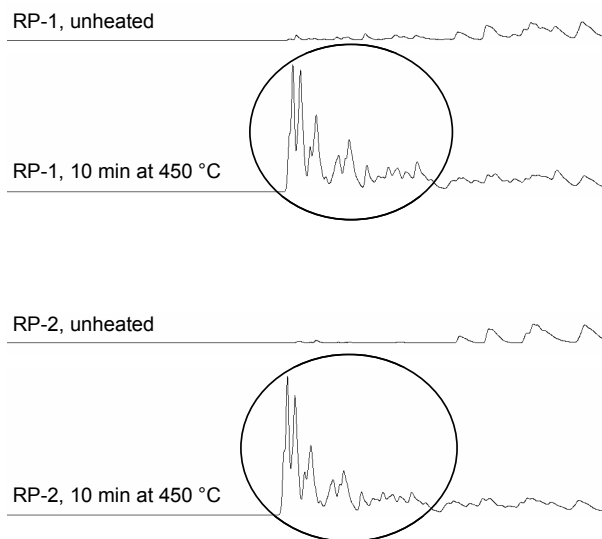


Figure 2. The Initial Part of the Chromatograms for Heated and Unheated RP-1 and RP-2.

COMPARISON OF THE THERMAL DECOMPOSITION KINETICS OF RP-1 AND RP-2

We monitored the increase in the suite of light decomposition products as a function of time, t , during the decomposition of RP-1 and RP-2. At each temperature, data were collected at

four different reaction times, with 3 to 5 replicate decomposition reactions run at each reaction time. These data were fit to a first-order rate law, equations 1–3, where $[B]_t$ is the concentration of products at time t and $[B]_\infty$ is the concentration of products at $t = \infty$:



$$-d[A]/dt = d[B]/dt = kt, \quad (2)$$

$$[B]_t = [B]_\infty(1 - \exp^{-kt}). \quad (3)$$

A pseudo-first-order rate constant for decomposition, k , was obtained from the fit. The half-life, $t_{0.5}$, at each temperature (i.e., the time required for one-half of the fuel to decompose) was then calculated from k by use of equation 4,

$$t_{0.5} = 0.6931/k. \quad (4)$$

A related quantity is the interval required for 1 % of the fuel to decompose, $t_{0.01}$. For first-order reactions, $t_{0.01}$ is calculated from the rate constant by use of eq 5,

$$t_{0.01} = 0.01005/k. \quad (5)$$

Finally, the rate constants for decomposition were used to evaluate the parameters of the Arrhenius equation, eq 6,

$$k = A \exp(-E_a/RT). \quad (6)$$

Figure 3 shows a plot of the corrected peak area (arbitrary units, see the Experimental) of the suite of light decomposition products as a function of time for the decomposition of RP-1 at 450 °C. The value of k was determined from the nonlinear fit to the data (shown as a solid line in Figure 3). For RP-1 at 450 °C, $k = 5.84 \times 10^{-4} \text{ s}^{-1}$ with an uncertainty of $1.33 \times 10^{-4} \text{ s}^{-1}$. The decomposition rate constants for RP-1 at all four temperatures, along with values of $t_{0.5}$ and $t_{0.01}$, are presented in Table I. The uncertainty for each value of k in Table I is simply the standard error in the nonlinear fit. The values of $t_{0.01}$ show that an apparatus residence time of approximately 15 min may be acceptable for property measurements at 375 °C. On the other hand, at 450 °C, residence times longer than 0.3 min may be unacceptable.

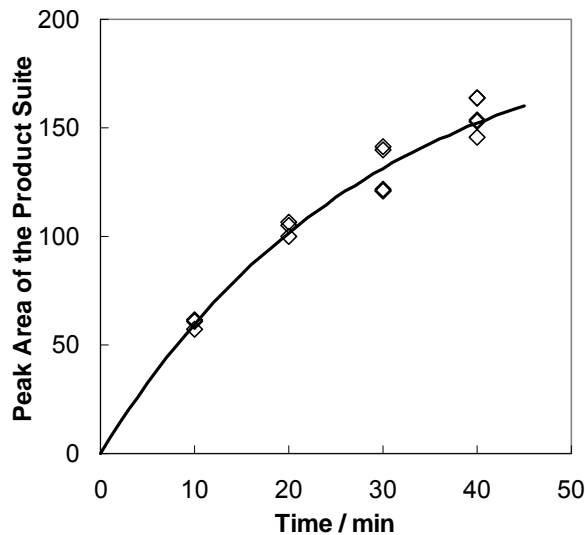


Figure 3. A Plot of the Kinetic Data for RP-1 at 450 °C.

Figure 4 shows a plot of the corrected peak area of the emergent product suite as a function of time for the decomposition of RP-2 at 450 °C. The value of k , again determined from

the nonlinear fit to the data, was $5.47 \times 10^{-4} \text{ s}^{-1}$ with a standard uncertainty of $0.80 \times 10^{-4} \text{ s}^{-1}$. The decomposition rate constants for RP-2 at all four temperatures, along with values of $t_{0.5}$ and $t_{0.01}$, are presented in Table II. Again, the uncertainty for each value of k' in Table II is simply the standard error in the nonlinear fit.

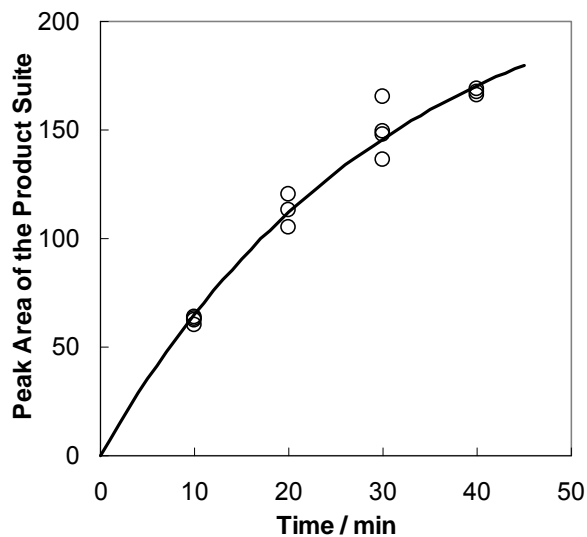


Figure 4. A Plot of the Kinetic Data for RP-2 at 450 °C.

A comparison of the rate constants in Tables I and II shows that the thermal stabilities of RP-1 and RP-2 are very similar. At every temperature except 425 °C, the rate constants for RP-1 and RP-2 are the same within their combined uncertainties (at 425 °C the rate constants differ by a little more than their combined standard uncertainties). From these data, we conclude that the thermal stabilities of RP-1 and RP-2 are not significantly different in the temperature range 375 °C to 450 °C, at least with respect to the formation of light, liquid-phase decomposition products.

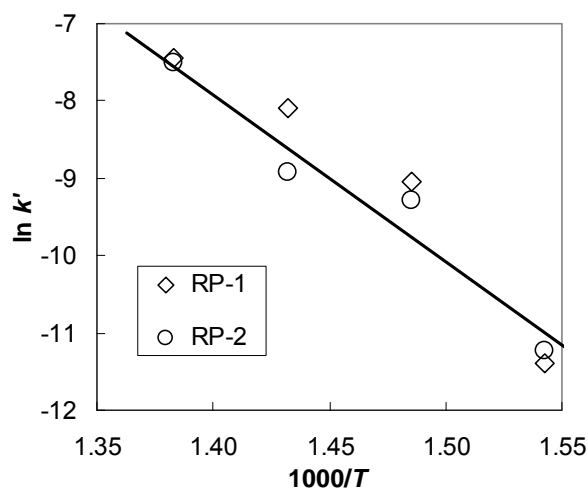
Table I. Kinetic Data for the Thermal Decomposition of RP-1.

RP-1				
$T / ^\circ\text{C}$	k' / s^{-1}	Uncertainty in k' / s^{-1}	$t_{0.5} / \text{h}^{-1}$	$t_{0.01} / \text{min}^{-1}$
375	1.13×10^{-5}	0.04×10^{-5}	17.0	14.8
400	1.19×10^{-4}	0.33×10^{-4}	1.62	1.41
425	3.08×10^{-4}	0.77×10^{-4}	0.63	0.54
450	5.84×10^{-4}	1.33×10^{-4}	0.33	0.29

Table II. Kinetic Data for the Thermal Decomposition of RP-2.

RP-2				
$T / ^\circ\text{C}$	k' / s^{-1}	Uncertainty in k' / s^{-1}	$t_{0.5} / \text{h}^{-1}$	$t_{0.01} / \text{min}^{-1}$
375	1.33×10^{-5}	0.30×10^{-5}	14.5	12.6
400	9.28×10^{-5}	2.01×10^{-5}	2.07	1.80
425	1.33×10^{-4}	0.33×10^{-4}	1.45	1.26
450	5.47×10^{-4}	0.80×10^{-4}	0.35	0.31

Figure 5 shows an Arrhenius plot of the rate constants for RP-1 and RP-2. The solid line in Figure 5 is a linear regression to the data for RP-2, which yields Arrhenius parameters of $A = 5.21 \times 10^9 \text{ s}^{-1}$ and $E_a = 180 \text{ kJ}\cdot\text{mol}^{-1}$. The uncertainty in E_a , calculated from the standard error in the slope of the regression, is $30 \text{ kJ}\cdot\text{mol}^{-1}$. Similarly, a linear regression to the data for RP-1 yields Arrhenius parameters of $A = 2.77 \times 10^{11} \text{ s}^{-1}$ and $E_a = 201 \text{ kJ}\cdot\text{mol}^{-1}$. The standard uncertainty in E_a is $39 \text{ kJ}\cdot\text{mol}^{-1}$. The relatively large uncertainties in the values of E_a are a reflection of the fact that the Arrhenius plots for RP-1 and RP-2 are not highly linear in the temperature range of these experiments. For both RP-1 and RP-2, the activation energy for decomposition is lower than the values reported for pure C10–C14 n-alkanes; for example, for n-dodecane E_a is $260 \text{ kJ}\cdot\text{mol}^{-1}$ (with a reported uncertainty of $8 \text{ kJ}\cdot\text{mol}^{-1}$).⁴⁹

**Figure 5. Arrhenius Plot for the Thermal Decomposition of RP-1 and RP-2.**

A decomposition study by MacDonald et al. at Stanford provides an important point of comparison.¹⁷ In that work, RP-1 and RP-2 were decomposed at temperatures of 827 °C to 1027 °C (1100 K to 1300 K) in an aerosol shock tube. In that temperature range, the decomposition rates for RP-1 and RP-2 were found to be quite similar.¹⁷ This important result, combined with our work, suggests that the decomposition rates (to light products) are similar over the entire temperature range of 375 °C to 1027 °C. It was also pointed out that a surprisingly linear Arrhenius plot can be made from the rate constants obtained at Stanford and at NIST, despite the fact that the rate constants from the two studies span eight orders of magnitude.¹⁷

RP-2 WITH ADDITIVES

For mixtures of RP-2 with additives, we again monitored the increase in the suite of light decomposition products as a function of time. At each temperature, data were collected at four different reaction times, with 3 to 5 replicate decomposition reactions run at each reaction time. Figure 6 shows the early part of the chromatograms obtained for unheated RP-2 and for thermally stressed samples of RP-2, RP-2+THQ, RP-2+tetralin, and RP-2+100. All of the thermally stressed samples had been heated at 375 °C for 6 h, and showed clearly differing amounts of decomposition (Figure 6). When compared to the chromatogram for thermally stressed RP-2, the chromatogram for RP-2+THQ shows almost no decomposition, the chromatogram for RP-2+tetralin shows significantly reduced decomposition, and the chromatogram for RP-2+100 shows little change in the amount of decomposition. Interestingly, the suite of decomposition products was essentially the same for each of the samples, and even the ratios of decomposition products were similar for each sample. Hence, it would appear that these additives slow the rate of decomposition without significantly altering the decomposition pathways.

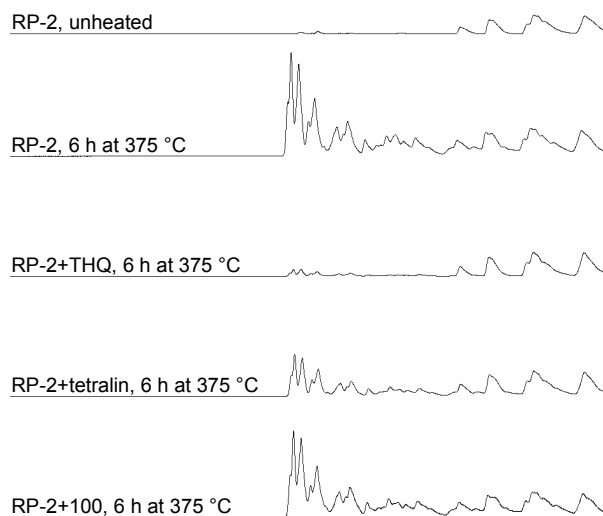


Figure 6. The Initial Part of the Chromatograms for RP-2 and RP-2 with Additives.

Figure 7 summarizes all of the kinetic data at 375 °C for neat RP-2 (○), RP-2+THQ (■), RP-2+tetralin (◆), and RP-2+100 (▲). For neat RP-2, after 6 h of thermal stress at 375 °C, the corrected peak area (see the EXPERIMENTAL) of the emergent product suite was 22.0 (with a standard deviation, σ , of 1.7). For comparison, the corrected peak areas after 6 h of thermal stress at 375 °C were 1.8 ($\sigma = 0.3$) for RP-2+THQ, 9.7 ($\sigma = 0.5$) for RP-2+tetralin, and 22.3 ($\sigma = 1.5$) for RP-2+100. In other words, the addition of 5 % THQ slowed the decomposition by approximately an order of magnitude, the addition of 5 % tetralin slowed the decomposition by approximately 50 %, and the addition of 256 mg/L of the +100 additive did not change the rate of decomposition. At longer reaction times, any stabilizing effect is smaller, presumably due to a decrease in the concentration of the stabilizer (see below). For example, after 24 h of thermal stress at 375 °C, the corrected peak areas were 58.6 ($\sigma = 4.0$) for neat RP-2, 8.1 ($\sigma = 1.8$) for RP-2+THQ, 41.3 ($\sigma = 3.5$) for RP-2+tetralin, and 54.9 ($\sigma = 3.9$) for RP-2+100. The trends observed at 375 °C were also seen at higher temperatures; for example, Figure 8 summarizes the kinetic data at 425 °C for neat RP-2 (○), RP-2+THQ (■), RP-2+tetralin (◆), and RP-2+100 (▲). Our general conclusions are that (1) 5 % THQ is the most effective stabilizer over the entire temperature range; (2) 5 % tetralin has a significant, but much smaller stabilizing effect; (3) the +100 additive has no significant effect at 256 mg/L; and (4) the stabilizing effect is greatest at the beginning of the reaction.

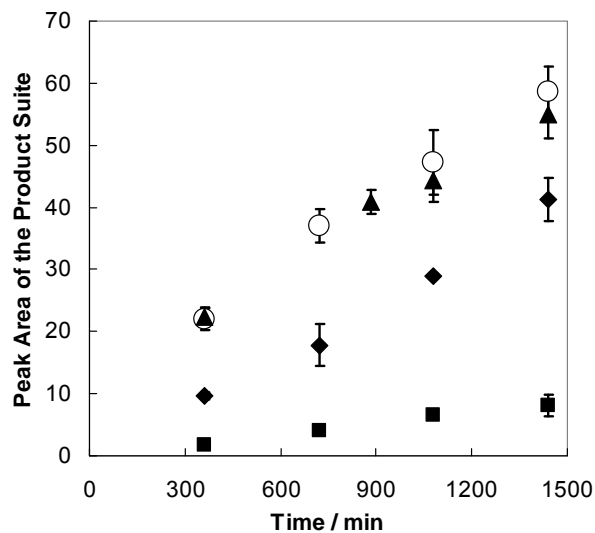


Figure 7. Kinetic Data for RP-2 with and without Additives at 375 °C.

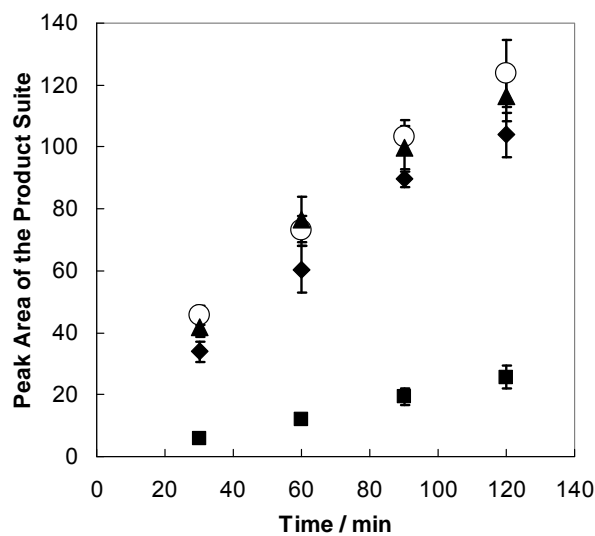


Figure 8. Kinetic Data for RP-2 with and without Additives at 425 °C.

Figure 9 shows a plot of the concentration of THQ as a function of reaction time. Even after 4 h at 425 °C, a small amount of the THQ remains. Approximately one half of the initial THQ remains after 2 h (the maximum reaction time shown in Figure 8). This is consistent with the fact that significant stabilization of the RP-2 is still observed after 2 h at 425 °C (Figure 8). It also shows that lower concentrations of THQ still provide effective stabilization of the fuel. Finally, the curve in Figure 9 is also consistent with our observation that the maximum stabilizing effect occurs at the beginning of thermal stress.

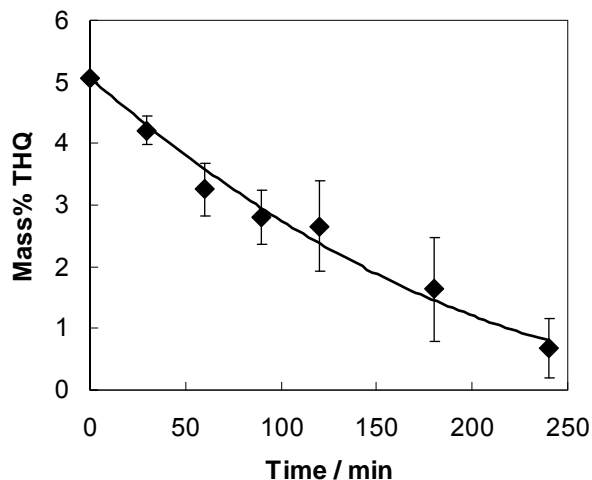


Figure 9. The mass % THQ remaining in the RP-2 as a function of time at 425 °C.

THQ is a stronger hydrogen donor than tetralin, so it is not surprising that it is a better thermal stabilizer for RP-2. Our results are consistent with work done on both jet fuel and biodiesel fuel where THQ was found to be a particularly good stabilizer.^{33,50} THQ is also known to stabilize RP-1 at temperatures below ~975 °C.¹⁷ The ineffectiveness of the +100 additive may not be due simply to its relatively low concentration, but rather to the high temperatures used in our experiments. The +100 additive was designed to work at temperatures of less than 220 °C, where autoxidation reactions (from oxygen dissolved in the fuel) are the dominant mechanism of fuel decomposition.²⁶ Therefore, it is not too surprising that it is less effective at inhibiting the cracking reactions that dominate at the temperatures studied herein. It is possible that the active components of the +100 additive simply decompose too quickly to be effective in this higher temperature regime.

SUMMARY AND CONCLUSIONS

Based on the formation of light, liquid-phase decomposition products, we found that there is no significant difference between the thermal stability of RP-1 and RP-2 at temperatures of 375 °C to 450 °C and an initial pressure of 34.5 MPa. This knowledge is useful for planning physical and chemical property measurements at high temperatures and pressures. THQ was the most promising of the additives studied. The addition of 5 % THQ decreased the rate of decomposition by approximately an order of magnitude. The addition of 5 % tetralin decreased the rate of decomposition by approximately 50 %. At the low concentration tested, the +100 additive did not significantly change the thermal stability of the RP-2. However, it is important to remember that the kinetics of decomposition may depend on the identity of the wetted surfaces of the apparatus. Strictly speaking, these results are best applied when the wetted surface is constructed from 300 series stainless steels.

FUTURE WORK

It would be interesting to study the effect of THQ concentration on the thermal stability of RP-2. Some other avenues for future work include testing more additives (e.g., decalin and benzyl alcohol) and testing different reactor materials (e.g., copper). Ultimately, it makes sense to study the most promising additives for their effect on coke formation.

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