

## Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 3. RP-2 with Varying Concentrations of the Stabilizing Additive 1,2,3,4-Tetrahydroquinoline

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The thermal stability of the kerosene-based rocket propellant RP-2 with varying concentrations of the stabilizing additive 1,2,3,4-tetrahydroquinoline (THQ) was investigated. The mixtures (by mass) were RP-2 + 0.1% THQ, RP-2 + 0.5% THQ, RP-2 + 1% THQ, and RP-2 + 5% THQ. These were thermally stressed in sealed stainless-steel reactors at 400 °C for 1–4 h. The approximate initial pressure at the reaction temperature was 34.5 MPa (5000 psi). The extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography. The results with each THQ mixture were compared to the thermal stability of neat RP-2 under the same conditions. The thermal stability of the mixtures showed a clear dependence upon the concentration of THQ. For example, the addition of 5% THQ slowed the rate of decomposition by approximately an order of magnitude, and the addition of 0.5% THQ slowed the rate of decomposition by approximately 50%. We also report the results of another potential stabilizing additive, *trans*-decahydronaphthalene (decalin). We tested the thermal stability of RP-2 + 5 mass % decalin at temperatures of 375, 400, 425, and 450 °C. Unlike THQ, the addition of 5% decalin to RP-2 had no significant effect on the thermal stability of RP-2 in this temperature range.

### Introduction

A kerosene-based rocket propellant serves the dual role of fuel and coolant in modern rocket engines.<sup>1,2</sup> 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 known as regenerative cooling, exposes the fuel to high temperatures. For this reason, the thermal stability of the fuel is important for its performance.<sup>1–9</sup>

A relatively new kerosene-based rocket propellant, RP-2, is intended to replace the rocket propellant RP-1, which has been in use for several decades. The specification for RP-2, along with an updated specification for RP-1, was published in 2006 as MIL-DTL-25576E. 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 red dye is not allowed in RP-2. All three of these differences were intended to increase the thermal stability of RP-2.

A promising approach for further improvements in the thermal stability of RP-2 is to use stabilizing additives.<sup>2</sup> The use of such additives has a long history with kerosene-based jet fuels.<sup>1,10</sup> Much of the work on jet fuels has focused on additives that are “hydrogen donors”, such as 1,2,3,4-tetrahydroquinoline

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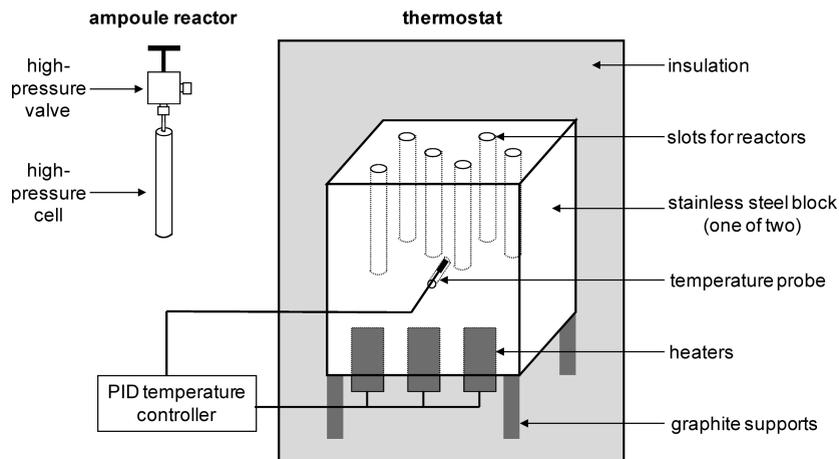
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**Figure 1.** Apparatus used to thermally stress the RP-2 and its mixtures.

(THQ),<sup>11–14</sup> 1,2,3,4-tetrahydronaphthalene (tetralin),<sup>11,13–19</sup> decahydronaphthalene (decalin),<sup>14,18,19</sup> and benzyl alcohol.<sup>13,14,20–22</sup> On the other hand, little work has been performed with stabilizing additives in kerosene-based rocket propellants.<sup>1,7,9</sup> To date, the most promising stabilizer is THQ, which has been shown to stabilize both RP-1 and RP-2 at a concentration of 5%.<sup>7,9</sup>

The goal of this study is to further investigate the finding that THQ significantly improves the thermal stability of RP-2. Herein, we report the relative thermal stabilities of mixtures of RP-2 with 0, 0.1, 0.5, 1, and 5% THQ (by mass). We found that significant stabilization is observed at THQ concentrations as low as 0.5%. All reactions were performed at 400 °C in stainless-steel ampoule reactors. The extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography (GC). In addition, we report that 5 mass % *trans*-decalin is ineffective as a stabilizer for RP-2 in the temperature range of 375–450 °C.

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## Experimental Section

**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 GC. THQ (98% purity) and decalin (99% purity) were also obtained from commercial sources and used as received. The RP-2, which was clear and colorless, was obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Edwards Air Force Base, CA).

**Apparatus.** A drawing of the thermostat and one of the reactors is shown in Figure 1. A detailed description of the apparatus has been published elsewhere (10.1021/ef900576g);<sup>8</sup> therefore, only an overview is provided here. Two thermostatted blocks of stainless steel were used to control the reaction temperature. A proportional–integral–derivative (PID) 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 two thermostatted blocks. Each reactor consisted of a tubular cell with a high-pressure valve. Each cell was made from ultrahigh-pressure 316L stainless-steel tubing, which was connected to a valve with a short length of narrow-diameter 316L stainless-steel tubing. The valve bodies were stainless-steel, and the packings were flexible graphite. The internal volume of each cell (approximately 0.11 mL) was determined gravimetrically from the mass of toluene required to fill it.

**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 of the decomposition reactions.<sup>23</sup> This is important because it helps ensure that differences in observed decomposition rates are only due to differences in temperature and composition (and not differences in pressure). With an equation of state for *n*-dodecane,<sup>24</sup> a computer program<sup>25</sup> calculated the mass of *n*-dodecane needed to achieve a pressure of 34.5 MPa at a given reaction temperature and cell volume. We then assumed that the same mass of RP-2 + additive would yield a pressure close to the target pressure. This is a reasonable assumption because, although RP-2 is a complex mixture, models derived from the properties of *n*-dodecane have been used successfully to approximate the physical properties of

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kerosene-based fuels.<sup>24,26</sup> The calculated mass of fuel was added to the cell with a syringe (sample masses were typically on the order of 0.06 g and varied depending upon the experimental temperature and cell volume). The valve was then affixed to the cell and closed. The cell was 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 reclosed, and the cell was warmed to room temperature. This single freeze–pump–thaw cycle removes 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, were avoided. Such procedures will change fuel composition by removing some of the more volatile components from the fuel. It is also worth mentioning that the autoxidation reactions caused by dissolved oxygen are thought to be relatively unimportant for hydrocarbon fuel decomposition above 300 °C.<sup>27</sup>

The loaded reactors were then inserted into the thermostatted stainless-steel block and maintained at the reaction temperature for a specified period ranging from 10 min to 24 h. To minimize the period required for temperature equilibration, only one reactor at a time was placed in the thermostatted block if the reaction period 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.<sup>28</sup> 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 below.

After each run, the cells and valves were rinsed extensively with a mixture of acetone and toluene. The cells were also sonicated for a few minutes (while filled with the acetone/toluene mixture) between rinsings to remove any solid deposits that may have formed on their walls. Cleaned cells and valves were heated to 110 °C for at least 8 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 not heated above room temperature. After a day, the fuel in the cell was removed and analyzed by GC (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 the absence of decomposition products in the resulting gas chromatogram.

**Analysis of Liquid-Phase Decomposition Products by GC.** Because of the production of light decomposition products, the reactors contained a pressurized mixture of vapor and liquid following thermal stress of the fuel. Because liquid-phase decomposition products were used to monitor the extent of decomposition, a sampling procedure was designed to minimize the 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 thermally stressed samples. The valve was then removed from the reactor, and any liquid remaining in the cell was transferred to the glass vial by use of a 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). Then, the liquid sample was immediately

diluted with a known amount of *n*-dodecane and refrigerated (at 7 °C) 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 (see below).

Aliquots (3  $\mu$ L) 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  $\mu$ m film of (5% phenyl)-methylpolysiloxane.<sup>29</sup> A temperature program was used that 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.

Decomposition of RP-2 was observed from the total increase in the chromatographic peak areas of a suite of light decomposition products. Chromatograms of unheated RP-2 (including RP-2 mixtures with the additives) 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 of this suite of decomposition products was used to measure the extent of decomposition. The peak area was corrected for dilution in *n*-dodecane by multiplying by the dilution factor. The peak area was 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 fuel samples. These corrected peak areas (in arbitrary units) were used to compare the effectiveness of each additive. The simple use of peak area for the comparison is possible because of the types of compounds being analyzed and the use of a FID. For hydrocarbons, the relative sensitivity of the detector (on the basis of moles of carbon) varies by only a few percentages.<sup>30</sup> Consequently, calibrating the detector for each individual compound is not expected to significantly change the comparisons.

## Results and Discussion

The thermal decomposition of fuels, such as RP-2, is very complex. There are a large number of compounds in the fuel, and 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, some type of simplifying assumption is necessary to gain insight into the overall thermal stability of such a fuel. In this work, we assume that a suite of light, liquid-phase decomposition products (see Figure 2) is representative of all of the decomposition products. This assumption is convenient for two reasons. First, the light decomposition products are produced in relative abundance. Second, the chromatographic peaks for these decomposition products occupy a region of the chromatogram that is essentially devoid of peaks for the unstressed fuel; therefore, peak deconvolution is unnecessary. It would be possible but much less convenient to monitor heavier decomposition products.

Aliquots of neat RP-2, RP-2 + 5% THQ, RP-2 + 1% THQ, RP-2 + 0.5% THQ, and RP-2 + 0.1% THQ were thermally stressed in sealed stainless-steel reactors at 400 °C.

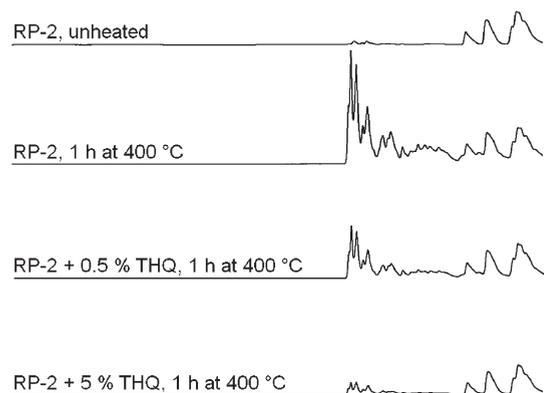
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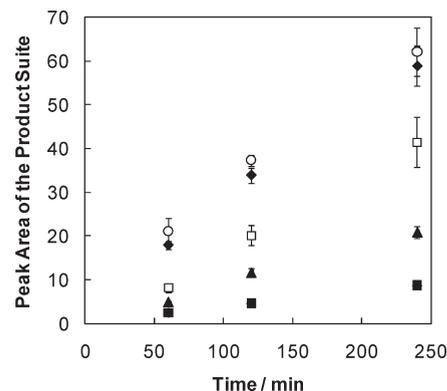
**Figure 2.** First 4 min of the gas chromatograms for several RP-2 samples. There are only a few peaks in this early part of the chromatogram for the sample of unheated RP-2. The suite of early eluting decomposition products is prominent in the chromatogram for the sample of RP-2 that had been thermally stressed at 400 °C for 1 h. The other two chromatograms are for mixtures of RP-2 with THQ and show clearly differing amounts of decomposition, with a clear dependence upon the concentration of the additive.

Reaction times ranged from 1 to 4 h. For all of the decomposition reactions, the approximate initial pressure at the reaction temperature was 34.5 MPa (5000 psi).

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 unheated RP-2 and thermally stressed samples of RP-2, RP-2 + 0.5% THQ, and RP-2 + 5% THQ. In comparison to the chromatogram for thermally stressed RP-2, the chromatogram for RP-2 + 0.5% THQ shows almost no decomposition and the chromatogram for RP-2 + 5% THQ shows significantly reduced decomposition (Figure 2). 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 THQ slows the rate of decomposition without significantly altering the decomposition pathways.

Figure 3 summarizes the data for all of the THQ mixtures, with plots of the corrected peak area (arbitrary units; see the Experimental Section) of the early eluting decomposition products as a function of time for each mixture. For neat RP-2, the corrected peak area after 1 h of thermal stress at 400 °C was 21.1 (with a standard deviation,  $s$ , of 3.0). For comparison, the corrected peak areas after 1 h at 400 °C were 8.1 ( $s = 1.0$ ) for RP-2 + 0.5% THQ and 2.4 ( $s = 0.4$ ) for RP-2 + 5% THQ. From this, we conclude that 5% THQ decreases the amount of decomposition by about an order of magnitude and 0.5% THQ decreases the amount of decomposition by a little more than 50%. At longer reaction times, the stabilizing effect is smaller, particularly for the lower concentrations of THQ. This is presumably caused by consumption of the stabilizer (10.1021/ef900577k).<sup>9</sup> The corrected peak areas for all of the measurements are given in Table 1.

Briefly, we also report the results of another potential stabilizing additive, decalin. We tested the thermal stability of RP-2 + 5% decalin at temperatures of 375, 400, 425, and 450 °C. Unlike THQ, the addition of 5% decalin to RP-2 had no significant effect on the thermal stability of RP-2 in this temperature range. To illustrate, Figure 4 compares the thermal stability of neat RP-2 and RP-2 + 5% decalin at 400 °C.

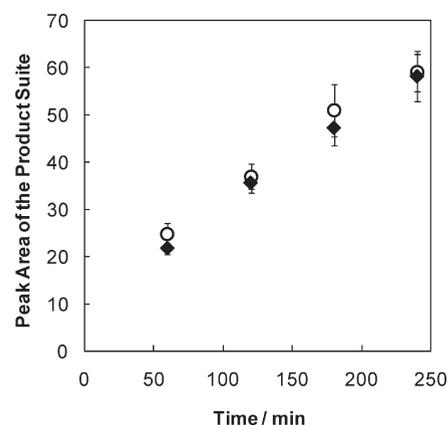


**Figure 3.** Plot of the corrected chromatographic peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 400 °C. The five different samples are ○, neat RP-2; ◆, RP-2 + 0.1% THQ; □, RP-2 + 0.5% THQ; ▲, RP-2 + 1% THQ; and ■, RP-2 + 5% THQ. The error bars indicate the standard deviation in 3–5 replicate decomposition reactions at each time point.

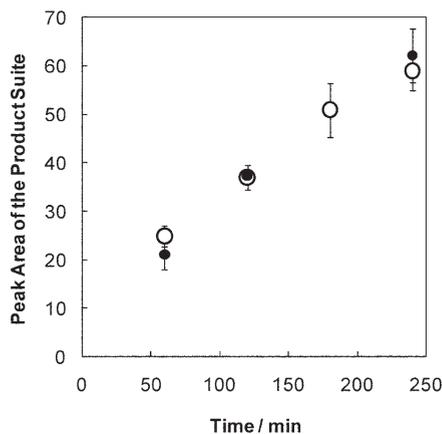
**Table 1.** Extent of Decomposition at 400 °C, as Judged by the Chromatographic Peak Area of the Product Suite, For Mixtures of RP-2 and THQ

percent THQ (%) <sup>a</sup>	period (min) <sup>b</sup>	peak area <sup>c</sup>	$s^d$
0	60	21.1	3.0
0	120	37.3	1.3
0	240	62.1	5.5
0.1	60	17.9	1.0
0.1	120	33.9	1.7
0.1	240	58.9	4.6
0.5	60	8.1	1.0
0.5	120	20.1	2.3
0.5	240	41.4	5.7
1	60	5.0	0.1
1	120	11.6	1.0
1	240	20.9	1.4
5	60	2.4	0.4
5	120	4.6	0.5
5	240	8.7	1.0

<sup>a</sup>The mass percent of THQ added to RP-2 as a stabilizer. <sup>b</sup>The period of thermal stress at 400 °C. <sup>c</sup>The mean corrected peak area of the product suite. <sup>d</sup>The standard deviation in the peak area.

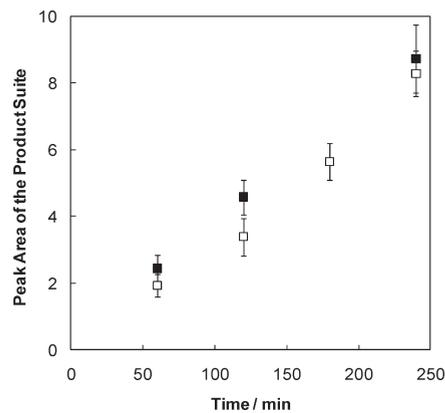


**Figure 4.** Plot of the corrected chromatographic peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 400 °C. The two samples are ○, neat RP-2; and ◆, RP-2 + 5% decalin. The error bars indicate the standard deviation in 3–5 replicate decomposition reactions at each time point.



**Figure 5.** Plot of the corrected chromatographic peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 400 °C. Both data sets are for the same batch of (neat) RP-2, but they were collected about 1 year apart with different reactors. The error bars indicate the standard deviation in 3–5 replicate decomposition reactions at each time point. These data illustrate the excellent reproducibility of the thermal stability measurement.

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, which would cause an apparent shift in the thermal stability of the RP-2 and its mixtures. Our experimental design accounts for such a possibility in the following ways. First, at any one time, we have a set of about 15 reactors that are used for thermal stability studies. Individual reactors occasionally fail (by developing a leak, etc.) and are replaced by new reactors. Consequently, the reactors used for any thermal stability study are of varying ages. Second, the different reaction periods and temperatures are performed in a randomized order. Consequently, any effects of reactor aging should be observable as scatter in the data (and, therefore, included in the uncertainty estimates). To verify this, we have also checked the repeatability of the kinetic plots over time. For example, we have already published thermal stability data at 400 °C for neat RP-2 (10.1021/ef900576g).<sup>8</sup> For the study reported herein, we repeated most of those measurements about 1 year later with an entirely different set of reactors. Both sets of data are shown in Figure 5, and they are in excellent agreement. Similarly, we have also published thermal stability data at 400 °C for RP-2 + 5% THQ (10.1021/ef900577k).<sup>9</sup> Here again, we repeated most of those measurements about 1 year later with an entirely different set of reactors. Both sets of data



**Figure 6.** Plot of the corrected chromatographic peak area of the early eluting decomposition products as a function of time. These data are for thermal stress at 400 °C. Both data sets are for RP-2 + 5% THQ, but they were collected about 1 year apart with different reactors. The error bars indicate the standard deviation in 3–5 replicate decomposition reactions at each time point. These data illustrate the excellent reproducibility of the thermal stability measurement.

are shown in Figure 6, and they are also in excellent agreement. From all of this evidence, we conclude that surface aging in the reactors is not very important in this system, which also suggests that surface catalysis is not very important in this system.

## Conclusions

With a clear dependence upon concentration, the additive THQ significantly increases the thermal stability of RP-2 with respect to the formation of light decomposition products (i.e., cracking). Significant stabilization was observed at concentrations as low as 0.5%. It would be interesting to test the effect of THQ on coke formation and in different reactor materials (e.g., copper). On the other hand, the addition of 5% decalin to RP-2 did not significantly change its thermal stability in the temperature range of 375–450 °C. Our ability to repeat the thermal stability measurements over time lends to a great deal of confidence in these results.

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