

# Thermal Stability of RP-2 as a Function of Composition: The Effect of Linear, Branched, and Cyclic Alkanes

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## S Supporting Information

**ABSTRACT:** The objective of this work was to identify compositional changes that could improve the thermal stability of the kerosene rocket propellant known as RP-2. For this study, we probed the effect of different types of alkanes on the thermal stability of RP-2. The proportion of linear, branched, or cyclic alkanes was increased by mixing RP-2 with one of the following alkanes (25% by mass): *n*-dodecane, *n*-tetradecane, 4-methyldodecane, 2,6,10-trimethyldodecane, or 1,3,5-triisopropylcyclohexane. These mixtures were thermally stressed in stainless steel ampule reactors at 673 K (400 °C, 752 °F) for up to 4 h. After each reaction, the stressed fuel was analyzed by gas chromatography with flame ionization detection. The decomposition kinetics of each added alkane was determined from the decrease in its chromatographic peak. The overall decomposition kinetics of each fuel mixture was determined from the increase in a suite of chromatographic peaks that correspond to light decomposition products. These data are compared to similar data for neat RP-2.

## INTRODUCTION

The thermal stability of kerosene-based rocket propellants is important for their performance because the rocket propellant serves as both the fuel and the coolant in the rocket engine.<sup>1–14</sup> Prior to combustion, some portion of 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, which is known as regenerative cooling, exposes the fuel to high temperatures. For this reason, the thermal stability of the kerosene rocket propellants RP-1<sup>1–10,13,14</sup> and RP-2<sup>3,5,10–14</sup> has been studied extensively. The specifications for the newer rocket propellant, RP-2, were published in 2006.<sup>15</sup> The most important differences between the specifications for RP-1 and RP-2 result in improved thermal stability for RP-2.

Another avenue that may yield additional improvement in the thermal stability of RP-2 is to change the overall chemical composition of the fuel. This is possible because RP-2 is blended from various refinery streams or feedstocks to meet specification requirements.<sup>16–19</sup> Therefore, in principle, it is possible to change the relative concentrations of various classes of hydrocarbons in the fuel. For example, it should be possible to increase (or decrease) the concentrations of linear alkanes, branched alkanes, or cyclic alkanes. This paper describes the first tests of such changes on the thermal stability of RP-2. The proportions of linear, branched, or cyclic alkanes were increased by mixing RP-2 with one of the following alkanes (25% by mass): *n*-dodecane, *n*-tetradecane, 4-methyldodecane, 2,6,10-trimethyldodecane, or 1,3,5-triisopropylcyclohexane. These mixtures were thermally stressed in stainless steel ampule reactors at 673 K (400 °C, 752 °F) for up to 4 h. The decomposition kinetics of the added alkane was monitored by gas chromatography. At the same time, the decomposition kinetics of the fuel mixture as a whole was determined from a

suite of chromatographic peaks that correspond to light, liquid-phase decomposition products.

## EXPERIMENTAL SECTION

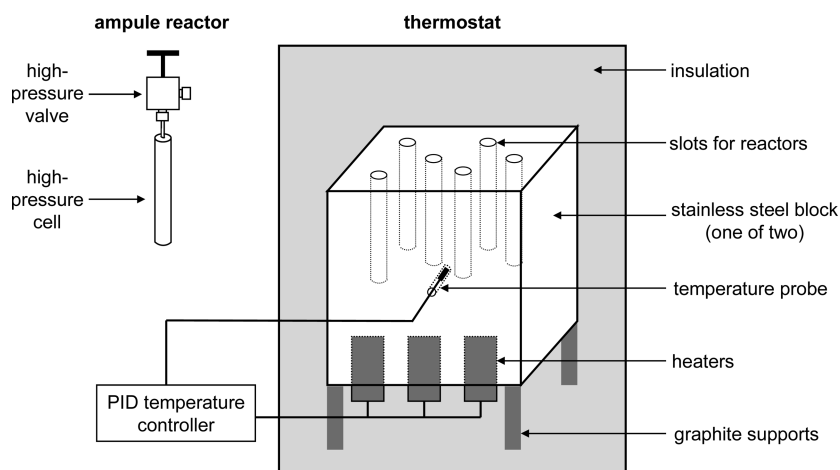
**Chemicals.** All solvents were obtained from commercial sources and used as received. They had purities of no less than 99%, as demonstrated by in-house gas chromatography with flame ionization detection (GC-FID). The *n*-dodecane (99%), *n*-tetradecane (99%), 4-methyldodecane (98%), and 2,6,10-trimethyldodecane (95%) were also obtained from commercial sources, and their purities were verified by GC-FID. They were then used as received. The 1,3,5-triisopropylcyclohexane (97%) was obtained from a commercial custom synthesis laboratory and was used as received after extensive chemical and thermophysical property characterization.<sup>20</sup> The RP-2 was obtained from the Combustion Devices Branch of the Air Force Research Laboratory (AFRL, Edwards Air Force Base), from a batch known as RP-2-EAFB. This is the same batch of RP-2 that was used for previous studies of thermal stability,<sup>10–14</sup> thermophysical property measurements,<sup>16,18,21</sup> and thermophysical model development.<sup>22</sup>

**Apparatus.** The apparatus used for the thermal stability measurements is shown in Figure 1. A detailed description of the apparatus is available elsewhere<sup>10</sup> and has been reproduced in the Supporting Information for the convenience of the reader. In short, the apparatus consists of a high-temperature thermostat and several small-volume reactors made from stainless steel.

**Decomposition Reactions.** The procedure used to fill the reactors was essentially identical to the one used for previous thermal stability studies on RP-2<sup>10–12</sup> and was designed to limit differences in the initial pressure for all of the decomposition reactions.<sup>1</sup> This is important because pressure can affect the observed rate constants for decomposition.<sup>23,24</sup> First, an equation of state for *n*-dodecane was used to calculate the mass of *n*-dodecane needed to achieve a pressure of 34.5 MPa (5000 psi) at a given temperature and reactor volume.<sup>25,26</sup> That same mass of RP-2 (or RP-2 mixture) was then added to the reactor. We originally chose *n*-dodecane as the model compound for

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

multiple reasons. Most importantly, its molar mass is similar to the average molar mass of the compounds in RP-2, and a good equation of state was available for *n*-dodecane.<sup>25,27</sup> For consistency with previous work, we continued to use this approach even though an equation of state model is now available for RP-2.<sup>22</sup> Interestingly, the equation of state model for RP-2 gives an initial reaction pressure of only 16.8 MPa (2440 psi) for these experiments, which is quite a bit lower than the estimated value from the equation of state for *n*-dodecane.

The calculated amount of RP-2 or RP-2 mixture (about 0.06 g) was added to the reactor. The fuel in the reactor was then subjected to a single freeze–pump–thaw cycle.<sup>10–12</sup> Next, the reactors were placed in the high-temperature thermostat for a reaction period that ranged from 1 to 4 h. The thermal equilibration period has been estimated to be 2 min for this apparatus under similar conditions.<sup>28</sup> After the reaction period, each reactor was immediately cooled to room temperature in a water bath, and the thermally stressed fuel mixture was analyzed as described below. Between reactions, the reactors were cleaned with our established procedure.<sup>10–12</sup> Briefly, the reactors were sonicated to remove solid deposits, rinsed with hexane and acetone, and heated to 100 °C for at least 12 h. Blank experiments were performed to confirm that the cells were dry at this point. 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 (the success of the drying procedure was confirmed by the absence of solvent in the resulting gas chromatogram).

**Analysis of the Thermally Stressed Fuel by Gas Chromatography.** The liquid phase of the thermally stressed fuel was analyzed by GC-FID. Except as detailed below, we used the same sample handling and analytical procedures as reported previously (two key paragraphs are reproduced in the Supporting Information for the convenience of the reader).<sup>10</sup>

Chromatograms of the unheated fuel mixtures exhibited only minor peaks with retention times of less than ~2.5 min; however, following thermal stress, the liquid phase contained several decomposition products that eluted earlier than 2.5 min. The corrected<sup>10</sup> total peak area of these light, liquid-phase decomposition products was used to monitor the thermal stability of the fuel as a whole. The simple use of peak area is possible because, for hydrocarbons, the relative sensitivity of the flame ionization detector (based on moles of carbon) varies by only a few percent.<sup>29</sup> Consequently, calibration of the detector for each individual compound would not improve the comparisons of fuel or additive stability.

As part of the same chromatographic analysis, we also monitored the decomposition kinetics of the added alkane. The chromatographic peak for the added alkane was corrected<sup>10</sup> for dilution and drifts in detector response. The relative area fraction was then calculated by dividing the corrected peak area by the original peak area (i.e., before thermal stress).

## RESULTS AND DISCUSSION

Aliquots of RP-2, or a mixture of RP-2 with an added alkane, were thermally stressed in stainless steel ampule reactors at a reaction temperature of 673 K (400 °C, 752 °F). This temperature was chosen in part because it allowed for convenient reaction periods of time—specifically, reaction periods of 1 to 4 h were used to determine the kinetics of decomposition. The thermally stressed liquid phase of every decomposition reaction was analyzed by GC-FID. For each fuel sample, kinetic data were collected at four different reaction periods, with three or four replicate decomposition reactions for each reaction period.

For the RP-2 mixtures, we monitored the decomposition kinetics of both the added alkane and the fuel as a whole. Following common practice,<sup>30</sup> a first-order rate law was assumed for the thermal decomposition reaction:



$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A] \quad (2)$$

The half-life (i.e., the period required for half of the fuel to decompose),  $t_{0.5}$ , was then calculated from  $k$  using eq 3:

$$t_{0.5} = \frac{0.6931}{k} \quad (3)$$

A related quantity is the interval required for 1% of the fuel to decompose,  $t_{0.01}$ . For first-order reactions,  $t_{0.01}$  can be calculated from  $k$  using eq 4:

$$t_{0.01} = \frac{0.01005}{k} \quad (4)$$

**Thermal Stability of the Added Alkanes.** For each RP-2 mixture, we measured the decomposition kinetics of the added alkane. This was a relatively simple task because the alkane additive was present at a much higher concentration (25% by mass) than any other component of the fuel mixture. For the kinetic measurement, we simply monitored the decrease in the corrected chromatographic peak area (see the Experimental Section) for the alkane additive as a function of time. With the assumption of a first-order rate law (eqs 1 and 2), the applicable equation is

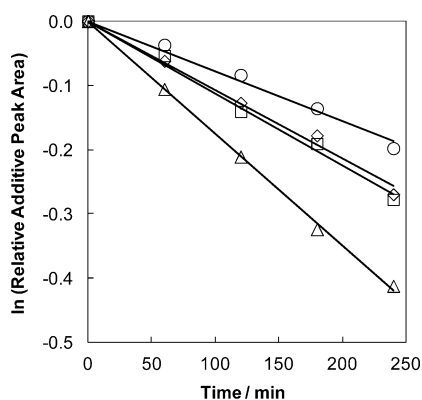
$$\ln([A]_t/[A]_0) = -k_{\text{additive}}t \quad (5)$$

where  $[A]_t$  is the concentration of alkane additive at time  $t$ ,  $[A]_0$  is the initial concentration of the alkane additive, and  $k_{\text{additive}}$  is the rate constant for the decomposition of the alkane additive. Thus, the value of  $k_{\text{additive}}$  was obtained from the slope of the plot of the linearized kinetic data. The values of  $k_{\text{additive}}$  along with the corresponding values of  $t_{0.5}$  and  $t_{0.01}$ , are presented in Table 1. The uncertainty for each value of  $k_{\text{additive}}$  in Table 1 is the standard error in the slope of the least-squares curve-fit.

**Table 1. Kinetic Data for Thermal Decomposition of the Alkane Additives at 400 °C**

additive	$k_{\text{additive}}/10^{-5} \text{ s}^{-1}$	$t_{0.5}/\text{h}$	$t_{0.01}/\text{min}$
<i>n</i> -tetradecane	$1.77 \pm 0.06$	10.9	9.49
4-methyl-dodecane	$1.86 \pm 0.09$	10.4	9.01
2,6,10-trimethyl-dodecane	$2.92 \pm 0.10$	6.60	5.75
1,3,5-triisopropylcyclohexane	$1.29 \pm 0.07$	14.9	13.0

Figure 2 summarizes the kinetic data for the decomposition of all of the added alkanes except *n*-dodecane. The most stable



**Figure 2.** Kinetic data for the decomposition of 1,3,5-triisopropylcyclohexane (O), *n*-tetradecane (◇), 4-methyl-dodecane (□), and 2,6,10-trimethyl-dodecane (△) at 400 °C. The error bars have been omitted for clarity. The solid lines are linear fits to the data with the assumption of a first-order rate law.

alkane additive is 1,3,5-triisopropylcyclohexane (represented by the circles in Figure 2). The least stable alkane additive is 2,6,10-trimethyl-dodecane (represented by the triangles in Figure 2). The overall difference in half-life observed for these two compounds is about a factor of 2.3. The stabilities of *n*-tetradecane (diamonds) and 4-methyl-dodecane (squares) are intermediate and are not significantly different from each other. We did not determine the stability of *n*-dodecane because the chromatographic solvent interfered with such an analysis.

The thermal stability of saturated hydrocarbons has been the subject of much research,<sup>23,24</sup> and certain stability trends have been observed for the pure compounds. For example, in comparison with normal alkanes, the presence of tertiary carbons (from branching) decreases the thermal stability (i.e., increases the rate constant for decomposition).<sup>24</sup> We observed this trend among the alkanes that were added to RP-2; the rate constants increased as the extent of tertiary branching increased (compare the results for *n*-tetradecane, 4-methyl-dodecane, and 2,6,10-trimethyl-dodecane in Table 1). However, the compound with the greatest number of tertiary carbons, 1,3,5-triisopropylcyclohexane, is actually the most stable, but that can be

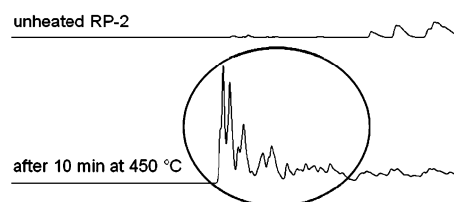
attributed to the expected high stability of cyclohexane rings.<sup>23,28</sup>

The thermal stability of linear alkanes has been particularly well studied, which allows for a comparison of rate constants for decomposition. In one such study, the first-order rate constant for the thermal decomposition of pure *n*-tetradecane was reported to be  $1.22 \times 10^{-5} \text{ s}^{-1}$  at 400 °C.<sup>31</sup> In another study, it was reported to be  $(1.78 \pm 0.06) \times 10^{-5} \text{ s}^{-1}$  at 400 °C.<sup>32</sup> One must be cautious when comparing rate constants obtained at different reaction pressures,<sup>23,24</sup> but it is worth noting that the two literature rate constants for pure *n*-tetradecane agree well with the value we obtained for the decomposition of *n*-tetradecane in a mixture with RP-2 (Table 1).

In another literature study,<sup>33</sup> the thermal stability of pure 1,3,5-triisopropylcyclohexane was studied under conditions essentially identical to those used in this study. The first-order rate constant for the thermal decomposition of pure 1,3,5-triisopropylcyclohexane was reported to be  $(1.34 \pm 0.05) \times 10^{-5} \text{ s}^{-1}$  at 400 °C,<sup>33</sup> which is identical to the value that we obtained for the decomposition of 1,3,5-triisopropylcyclohexane in a mixture with RP-2 (Table 1).

Although we studied only a limited number of (RP-2 + alkane) mixtures, it is encouraging that the literature trends observed for pure alkanes also appeared to hold for alkanes in the fuel mixtures. Therefore, a preliminary conclusion is that rate constants and trends from the literature for hydrocarbon stability can be utilized when blending a batch of RP-2. For example, decreasing the proportion of tertiary carbons should increase the thermal stability of the fuel. It should also be possible to increase the stability of the fuel by increasing the proportion of cyclohexane rings or quaternary carbons.<sup>23,24</sup>

**Overall Thermal Stability of RP-2 and Its Mixtures with Added Alkanes.** The thermal decomposition of fuels such as RP-2 is complex. There are many 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, simplifying assumptions are necessary in order to gain insight into the overall thermal stability of such a fuel. One important assumption that was made in this work is that only a subset of decomposition products could be used to monitor the kinetics of fuel decomposition. For convenience, a suite of light, liquid-phase decomposition products was used. In Figure 3, which shows the early parts of the chromatograms obtained for thermally stressed and unstressed RP-2, it can be seen that this suite of decomposition products occupied a region of the chromatogram that was essentially vacant for the unheated fuel, which greatly simplified the data analysis.



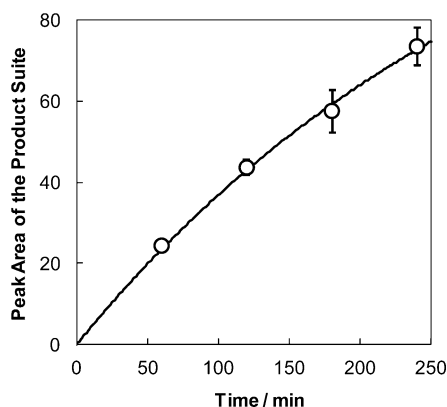
**Figure 3.** Initial parts of the chromatograms for (top) unheated and (bottom) thermally stressed RP-2. The suite of light, liquid-phase decomposition products (circled) that developed with thermal stress was used to monitor the stability of the fuel as a whole.

A second, important, simplifying assumption was the use of a first-order rate law to fit the kinetic data for product formation. Hence, the applicable equation is

$$[B]_t = [B]_\infty(1 - e^{-k't}) \quad (6)$$

where  $[B]_t$  is the concentration of products at time  $t$ ,  $[B]_\infty$  is the concentration of products at  $t = \infty$ , and  $k'$  is a pseudo-first-order rate constant for the decomposition of the fuel as a whole. The data for the light, liquid-phase decomposition products were fitted to eq 6 with a nonlinear least-squares regression routine, and the value of  $[B]_\infty$  was treated as a floating variable. With this approach, at low conversions, the value of  $k'$  is most heavily influenced by the least stable components of the fuel.

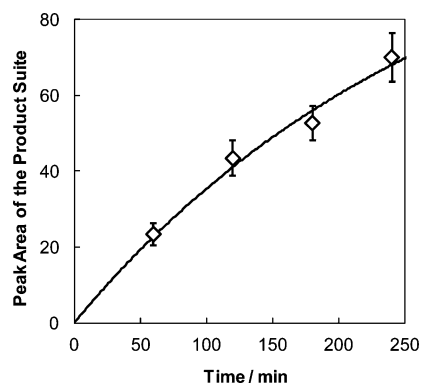
Figure 4 shows a plot of the corrected peak area (arbitrary units; see the Experimental Section) of the suite of light



**Figure 4.** Plot of the corrected peak area of the early-eluting decomposition products as a function of time. These data are for thermal stress of neat RP-2 at 400 °C. The error bars show the standard deviations in replicate decomposition reactions. The solid line is a nonlinear fit to the data with the assumption of a first-order rate law.

decomposition products as a function of time for the decomposition of neat RP-2 at 400 °C. The value of  $k'$  was determined from the nonlinear fit to the data (shown as a solid line in Figure 4). For neat RP-2 at 400 °C,  $k' = 5.1 \times 10^{-5} \text{ s}^{-1}$  with a standard uncertainty of  $1.5 \times 10^{-5} \text{ s}^{-1}$ . We measured the thermal stability of mixtures of RP-2 with linear, branched, or cyclic alkanes by the same method that was used for neat RP-2. For example, Figure 5 shows the kinetic data for the mixture of 75% RP-2 and 25% *n*-tetradecane by mass. The kinetic curves in Figures 4 and 5 are quite similar. Indeed, for the mixture of RP-2 and *n*-tetradecane,  $k' = 5.9 \times 10^{-5} \text{ s}^{-1}$  with a standard uncertainty of  $2.2 \times 10^{-5} \text{ s}^{-1}$ , which is not significantly different from the rate constant for neat RP-2. The decomposition rate constants for all of the RP-2 mixtures, along with values of  $t_{0.5}$  and  $t_{0.01}$ , are presented in Table 2. The uncertainty for each value of  $k'$  in Table 2 is the standard error in the nonlinear fit of the kinetic data.

The obvious conclusion from the data in Table 2 is that the rate constant for the decomposition of neat RP-2 is not significantly different from the rate constants for any of the mixtures. At first glance this may seem surprising because the added alkanes did decompose at significantly different rates (see Table 1). However, we believe that there are three factors that account for this result and illustrate the difficulty of



**Figure 5.** Plot of the corrected peak area of the early-eluting decomposition products as a function of time. These data are for thermal stress of 75% RP-2 + 25% *n*-tetradecane at 400 °C. The error bars show the standard deviations in replicate decomposition reactions. The solid line is a nonlinear fit to the data with the assumption of a first-order rate law.

**Table 2.** Kinetic Data for the Thermal Decomposition of RP-2 and Its Mixtures at 400 °C

fuel	$k'/10^{-5} \text{ s}^{-1}$	$t_{0.5}/\text{h}$	$t_{0.01}/\text{min}$
neat RP-2	$5.1 \pm 1.5$	3.7	3.3
75% RP-2 + 25% <i>n</i> -dodecane	$6.3 \pm 2.1$	3.0	2.7
75% RP-2 + 25% <i>n</i> -tetradecane	$5.9 \pm 2.2$	3.3	2.8
75% RP-2 + 25% 4-methyldodecane	$5.2 \pm 1.9$	3.7	3.2
75% RP-2 + 25% 2,6,10-trimethyldodecane	$6.9 \pm 2.0$	2.8	2.4
75% RP-2 + 25% 1,3,5-triisopropylcyclohexane	$6.8 \pm 2.6$	2.8	2.5

establishing the “global” stability of a complex mixture such as RP-2.

First, the relative standard uncertainties in the values of  $k'$  are large, ranging from 29% to 38%. Therefore, it is simply not possible to discern small changes in overall fuel stability. On the other hand, the relative standard uncertainties in  $k_{\text{additive}}$  range from 3% to 5% (see Table 1). Consequently, much smaller differences in stability are observable in that type of experiment.

Second, the added alkane simply dilutes the components of the original fuel instead of replacing certain components. Consequently, when a relatively stable alkane is added to the RP-2, any increase in the stability of the mixture is necessarily small because all of the less stable components in RP-2 are still present. If a relatively unstable alkane were added to the RP-2, a significant decrease in the stability of the mixture may be possible, but that was not the case for the alkanes studied herein (see below).

Third, the methodology used to determine the overall stability of the fuel is not equally sensitive to the decomposition products of all of the compounds. The region of the chromatogram used for the kinetic analysis of the fuel mixtures corresponds approximately to alkanes and alkenes with five to eight carbon atoms and to aromatics with six or seven carbon atoms. If components of the fuel do not produce decomposition products in that range (or if they produce unusually large amounts of decomposition products in that range), an erroneous conclusion about the thermal stability of the fuel mixture could be reached. A good example of this is the thermal decomposition of neat 1,3,5-triisopropylcyclohexane, which has been studied under very similar conditions.<sup>33</sup> For 1,3,5-triisopropylcyclohexane, only minor decomposition products



appear in the region of the chromatogram used for the kinetic analysis of the fuel mixtures; the sum of these minor products accounts for only about 5% of the liquid-phase decomposition products. By contrast, for a linear alkane like *n*-tetradecane, about half of liquid-phase decomposition products are alkanes or alkenes with five to eight carbon atoms.<sup>31,34</sup>

One must be cautious when comparing  $k_{\text{additive}}$  and  $k'$  because of the additional assumptions that were made in the determination of  $k'$ . Nevertheless, it is interesting to note that the values of  $k_{\text{additive}}$  are all at least a little smaller than the value of  $k'$  for neat RP-2. This suggests that RP-2 contains components that are less stable than any of the added alkanes that were tested. However,  $k_{\text{additive}}$  for 2,6,10-trimethyldodecane is only marginally smaller than  $k'$  for neat RP-2, so the presence of this type of highly branched alkane in RP-2 could account for its observed stability. In any case, determining the identities of the least-stable fuel components and minimizing them in the blending process appears to be essential for the creation of a more stable fuel.

## CONCLUSIONS

Initial tests of the thermal stability of different classes of alkanes in RP-2 mixtures were made. For the compounds tested, we observed the same stability trend for alkanes in the fuel mixtures as has been observed for the pure compounds. For 1,3,5-triisopropylcyclohexane in RP-2 and *n*-tetradecane in RP-2, even the rate constants for decomposition were found to be identical to (or similar to) values reported for the pure compounds. These are useful findings because they suggest that the extensive literature of hydrocarbon thermal stability can be brought to bear when choosing feedstocks for RP-2 blending. For example, it should be possible to improve the thermal stability of RP-2 by using feedstocks that contain a lower proportion of the least stable alkane bond types (e.g., tertiary carbons). Ideally, the least stable alkane bond types would be replaced with the most stable alkane bond types (such as quaternary carbons or cyclohexane rings). An increase in the proportion of quaternary carbons in the fuel is particularly intriguing because such compounds are also less likely to form coke. For future work, it would be useful to specifically identify the least stable components of RP-2, which would require a detailed study of the products of thermal stress. It would also be interesting to verify the stability trends observed herein with a high-flow-rate test bed that more closely mimics the conditions in a rocket engine.

## ASSOCIATED CONTENT

### Supporting Information

Detailed descriptions of (1) the apparatus used for thermal stability measurements and (2) the analysis of the thermally stressed fuel by gas chromatography. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Andersen, P. C.; Bruno, T. J. Thermal decomposition kinetics of RP-1 rocket propellant. *Ind. Eng. Chem. Res.* **2005**, *44*, 1670–1676.
- (2) Bates, R. W.; Edwards, T.; Meyer, M. L. Heat Transfer and Deposition Behavior of Hydrocarbon Rocket Fuels. 41st Aerospace Sciences Meeting and Exhibit; AIAA Paper 2003-123.
- (3) Brown, S. P.; Frederick, R. A. Laboratory-scale thermal stability experiments on RP-1 and RP-2. *J. Propul. Power* **2008**, *24*, 206–212.
- (4) Edwards, T.; Zabarnick, S. Supercritical Fuel Deposition Mechanisms. *Ind. Eng. Chem. Res.* **1993**, *32*, 3117–3122.
- (5) MacDonald, M. E.; Davidson, D. F.; Hanson, R. K. Decomposition Rate Measurements of RP-1, RP-2, *n*-Dodecane, and RP-1 with Fuel Stabilizers. 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; AIAA Paper 2008-4766.
- (6) Stiegemeier, B.; Meyer, M. L.; Taghavi, R. A. Thermal Stability and Heat Transfer Investigation of Five Hydrocarbon Fuels: JP-7, JP-8, JP-8 + 100, JP-10, RP-1. 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; AIAA Paper 2002-3873.
- (7) Wohlwend, K.; Maurice, L. Q.; Edwards, T.; Striebich, R. C.; Vangness, M.; Hill, A. S. Thermal stability of energetic hydrocarbon fuels for use in combined cycle engines. *J. Propul. Power* **2001**, *17*, 1258–1262.
- (8) Edwards, T. Liquid fuels and propellants for aerospace propulsion: 1903–2003. *J. Propul. Power* **2003**, *19*, 1089–1107.
- (9) Irvine, S. A.; Schoettmer, A. K.; Bates, R. W.; Meyer, M. L. History of Sulfur Content Effects on the Thermal Stability of RP-1 under Heated Conditions. 40th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; AIAA Paper 2004-3879.
- (10) Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 1. Comparison of RP-1 and RP-2. *Energy Fuels* **2009**, *23*, 5517–5522.
- (11) Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 2. RP-2 with Three Additives. *Energy Fuels* **2009**, *23*, 5523–5528.
- (12) Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of Kerosene-Based Rocket Propellants. 3. RP-2 with Varying Concentrations of the Stabilizer 1,2,3,4-Tetrahydroquinoline. *Energy Fuels* **2011**, *25*, 288–292.
- (13) Bruno, T. J.; Windom, B. C. Method and Apparatus for the Thermal Stress of Complex Fluids: Application to Fuels. *Energy Fuels* **2011**, *25*, 2625–2632.
- (14) Windom, B. C.; Bruno, T. J. Assessment of the Composition and Volatility of Thermally Stressed RP-1 and RP-2: Application to Fuel Regenerative Cooling. *Energy Fuels* **2011**, *25*, 5200–5214.
- (15) Military Specification MTL-DTL-25576E; 2006.
- (16) Ott, L. S.; Hadler, A. B.; Bruno, T. J. Variability of the Rocket Propellants RP-1, RP-2, and TS-5: Application of a Composition- and Enthalpy-Explicit Distillation Curve Method. *Ind. Eng. Chem. Res.* **2008**, *47*, 9225–9233.
- (17) Huber, M. L.; Lemmon, E. W.; Bruno, T. J. Effect of RP-1 Compositional Variability on Thermophysical Properties. *Energy Fuels* **2009**, *23*, 5550–5555.
- (18) Lovestead, T. M.; Windom, B. C.; Riggs, J. R.; Nickell, C.; Bruno, T. J. Assessment of the Compositional Variability of RP-1 and RP-2 with the Advanced Distillation Curve Approach. *Energy Fuels* **2010**, *24*, 5611–5623.
- (19) Billingsley, M.; Edwards, T.; Shafer, L. M.; Bruno, T. J. Extent and Impacts of Hydrocarbon Fuel Compositional Variability for

Aerospace Propulsion Systems. 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; AIAA Paper 2010-6824.

(20) Bruno, T. J.; Fortin, T. J.; Lovestead, T. M.; Widegren, J. A. Chemical and Thermophysical Characterization of 1,3,5-Triisopropylcyclohexane. *J. Chem. Eng. Data* **2012**, *57*, 2343–2349.

(21) Lovestead, T. M.; Bruno, T. J. A Comparison of the Hypersonic Vehicle Fuel JP-7 to the Rocket Propellants RP-1 and RP-2 with the Advanced Distillation Curve Method. *Energy Fuels* **2009**, *23*, 3637–3644.

(22) Huber, A. L.; Lemmon, E. W.; Ott, L. S.; Bruno, T. J. Preliminary Surrogate Mixture Models for the Thermophysical Properties of Rocket Propellants RP-1 and RP-2. *Energy Fuels* **2009**, *23*, 3083–3088.

(23) Fabuss, B. M.; Satterfield, C. N.; Kafesjian, R.; Smith, J. O. Thermal Decomposition Rates of Saturated Cyclic Hydrocarbons. *Ind. Eng. Chem. Process Des. Dev.* **1964**, *3*, 248.

(24) Fabuss, B. M.; Smith, J. O.; Satterfield, C. N. *Adv. Pet. Chem. Refin.* **1964**, *9*, 157–201.

(25) Lemmon, E. W.; Huber, M. L. Thermodynamic properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 960–967.

(26) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. In *NIST Standard Reference Database 23*, version 9.0; National Institute of Standards and Technology: Gaithersburg, MD, 2010.

(27) Huber, M. L.; Laesecke, A.; Perkins, R. Transport properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 968–975.

(28) Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of Propylcyclohexane. *Ind. Eng. Chem. Res.* **2009**, *48*, 654–659.

(29) McNair, H. M.; Bonelli, E. J. *Basic Gas Chromatography*; Varian: Palo Alto, CA, 1968.

(30) Edwards, T. Cracking and deposition behavior of supercritical hydrocarbon aviation fuels. *Combust. Sci. Technol.* **2006**, *178*, 307–334.

(31) Song, C. S.; Lai, W. C.; Schobert, H. H. Condensed-Phase Pyrolysis of *n*-Tetradecane at Elevated Pressures for Long Duration. Product Distribution and Reaction Mechanisms. *Ind. Eng. Chem. Res.* **1994**, *33*, 534–547.

(32) Yu, J.; Eser, S. Kinetics of supercritical-phase thermal decomposition of C<sub>10</sub>–C<sub>14</sub> normal alkanes and their mixtures. *Ind. Eng. Chem. Res.* **1997**, *36*, 585–591.

(33) Gough, R. V.; Widegren, J. A.; Bruno, T. J. Thermal Decomposition Kinetics of 1,3,5-Triisopropylcyclohexane. *Ind. Eng. Chem. Res.* **2013**, *52*, 8200–8205.

(34) Yu, J.; Eser, S. Thermal decomposition of C<sub>10</sub>–C<sub>14</sub> normal alkanes in near-critical and supercritical regions: Product distributions and reaction mechanisms. *Ind. Eng. Chem. Res.* **1997**, *36*, 574–584.