

Thermal Decomposition Kinetics of RP-1 Rocket Propellant

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As part of a thermophysical and transport property measurement project, the global decomposition kinetics of the kerosene-based rocket propellant, RP-1, was investigated. We measured the decomposition of RP-1 at elevated temperatures (that is, under thermal stress) as a function of time and then derived a global pseudo-first-order rate constant that describes the overall mixture decomposition. While not as rigorous as a component-by-component kinetics analysis, this approach is, nevertheless, instructive and can be used to guide the aforementioned property measurements. Decomposition measurements were made at 375, 400, 425, and 500 °C for two separate samples of RP-1. One sample was a typical batch, showing the expected fractions of paraffins, cycloparaffins, olefins, and aromatics. The other was an off-specification batch that had unusually high olefin and aromatic contents. Decomposition rate constants ranged from $6.92 \times 10^{-5} \text{ s}^{-1}$ at 375 °C to $1.07 \times 10^{-3} \text{ s}^{-1}$ at 500 °C. While the primary purpose of this work was to establish operating ranges for the property measurements, the results clearly have implications in other facets of RP-1 application. These applications include establishing operating ranges for supercritical fluid heat sink regimes, setting residence times in motors, etc. In addition to the decomposition kinetics, we have also done a chemical analysis of the vapor phase that is produced upon thermal stress. The vapor phase for this analysis was extracted using a new gas–liquid separator.

Introduction

Physical property data for rocket propellants are critical for engineering design and process development.¹ The properties that are required include equilibrium properties (such as the fluid density, heat capacities, etc., as a function of temperature and pressure) and transport properties (such as viscosity, thermal conductivity, etc., also as a function of temperature and pressure). In previous work, some of the properties of important kerosene-based rocket fuels have been studied.² As a result, surrogate fuel mixtures have been developed to provide a simplified mixture with components whose properties are well-characterized.^{3,4} These surrogates were then used for modeling.^{1,5} More recently, physical property measurements and models for these complex mixtures have become necessary at temperatures greater than 300 °C and pressures greater than 10 MPa, areas in which data are scarce.² Under these conditions, the possibility of decomposition of the fluid is a serious concern because this can affect both the performance and lifetime of physical property instrumentation and the validity of the data that are obtained.

It is important to assess the extent of decomposition of fuels (or any fluids) before and during physical property experiments.^{6,7} Changes in the composition of the fuel during thermal equilibration and measurement in an apparatus may lead to significant complications in the measurements. This will not necessarily preclude the measurements, but it certainly will affect the way in which the measurements are performed and perhaps interpreted. For example, the rate at which these fuels decompose may pose residence time constraints on

measurements conducted at high temperature and pressure.^{6–9} Thus, sample cycling and throughput rates in an experimental apparatus must be understood and planned before measurements commence. Furthermore, pressure ratings for the measurement equipment that are based on the unreacted fuel may be exceeded if significant decomposition of the fuel occurs. In some instances, extremely high (and hazardous) pressures can result from poorly or incompletely understood decomposition kinetics.

Rocket Propellant 1 (RP-1) is a long-established hydrocarbon fuel that continues to be widely used since it was first developed in the 1950s.¹⁰ RP-1 is produced from a narrow-range kerosene fraction that is further processed to reduce unsaturated compounds and also sulfur-containing hydrocarbons. Distillates from crude oil that are high in paraffinic stocks are generally used for RP-1 production in order to meet specifications for density, heat of combustion, and aromatic content.¹¹ Previous analyses of RP-1 have shown the fuel to be a complex mixture of compounds including paraffins, olefins, and aromatics.^{2,12}

Recent work on the physical properties of kerosene-based fuels has demonstrated the need to take explicit account of the possibility of chemical reactions occurring during the measurements.^{13,14} The formation of solid deposits (coking) has been thoroughly studied and reflects one aspect of the fuel decomposition, but few studies have been reported on the liquid decomposition of RP-1, where the composition of the fluid may change before the onset of coking. Significant changes in the composition of RP-1 were reported at temperatures below which deposit formation has been observed.¹³ Yet, it remains unclear as to what extent decomposition occurs under the high pressure and temperature. In this study, changes in the chemical composition of liquid

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RP-1 were investigated and correlated with exposure to thermal stress.

A number of experimental approaches designed to measure thermal decomposition have been developed at NIST.^{6,7} The data from these measurements have been used to place thermophysical property measurements into a proper context. This has often taken the form of an extrapolation to time = 0, such as with the measurement of pressure–volume–temperature (*PVT*) surfaces.^{8,9,15} While valid for the measurement and data set for which it was intended, this is limited in application to a particular apparatus (such as a *PVT* instrument). Clearly, a more satisfactory and generally applicable approach would be the measurement of a decomposition rate constant. This approach, even if approximate, would allow extension to other measurement and apparatus and would provide a predictive capability. For example, it may be important to measure the *PVT* surface, as well as some transport properties such as viscosity and thermal conductivity. Provided the instruments used to make each of the measurements are sufficiently similar in construction (that is, the wetted surfaces are made from similar materials), a measured decomposition rate constant would provide a valuable guide in the design of the overall measurement program. In this way, regimes of serious (or catastrophic) decomposition can be avoided. Thus, a *PVT* measurement cell constructed of 316 stainless steel would be expected to present the same (or very similar) chemical environment to the sample as the cells used for the measurements presented in this paper. One would then expect the onset of decomposition to follow the same trends revealed from this decomposition study.

In the case of complex fluids with many components, a reaction rate constant will necessarily be approximate and well-defined only for a particular mixture (that is, a particular composition). Here, it will describe not a single, well-understood reaction but a complex series of reactions.

To implement this approach, a measurement method to investigate the kinetics of liquid hydrocarbon decomposition at high temperature and pressure was developed. Using this approach, the thermal decomposition of RP-1 was investigated at a pressure of 35 MPa and temperatures from 375 to 500 °C. The increase in decomposition products (relative to the pure fuel) with time was monitored, and global decomposition rate constants were determined. From the rate constants, Arrhenius parameters were estimated for the prediction of rate constants at different temperatures.

Theory

For a simple reaction in which a starting material (A) thermally decomposes into a product (eq 1), perhaps the best description of the decomposition is the fundamental rate equation. For a model reaction where starting material A decomposes into product B (eq 1), the rate law can be written as eq 2 or 3, where [A] is the



$$\text{rate} = -d[A]/dt \quad (2)$$

$$\text{rate} = d[B]/dt \quad (3)$$

concentration of A, [B] is the concentration of B, and *t* is the time. As the reaction proceeds, the decrease in A (denoted by the negative sign) is accompanied by a

corresponding increase in B, and a rate equation can be expressed in terms of the reaction products as

$$\frac{d}{dt} [B] = k[B]^n \quad (4)$$

where *k* is the reaction rate constant and *n* is the order of the reaction. If we integrate the equation and assume first-order, we obtain

$$\ln [B] - \ln [B_0] = kt \quad (5)$$

where [B₀] is the initial product concentration, which at the start of a decomposition reaction is zero. A plot of [B] as a function of time will provide a straight line with a zero intercept, the slope of which is *k*.

An inherent limitation in defining the rate constant in terms of B occurs for disproportionate reactions, where each molecule of starting material decomposes to generate more than one molecule of product. A disproportionate reaction can be written as $A \rightarrow \Sigma B_i$, where B_{*i*} is the number of individual products formed in the reaction. In the thermal decomposition of a complex fluid such as a kerosene, the potential for such a situation is clear. Furthermore, the decomposition rate of a single component can be significantly altered in the presence of the mixture compared to that of the pure component.¹⁶ Nevertheless, insight can be gained into the overall fluid stability against thermal stress by focusing instead on the global behavior of the bulk fluid. Then, if the trends in the measured data are appropriate, the decomposition can be approximated as first-order decomposition.¹⁷ Thus, rather than describing the decomposition of each component in the mixture, a global rate constant can be used to describe the bulk behavior of the complex fluid.^{18,19}

While the assumption of a first-order rate law provides a useful starting point in determining the global rate constant, not all reactions can be adequately described by a first-order expression. This is clear with complex reactions, where the initial decomposition products may themselves undergo subsequent thermal decomposition. Therefore, the validity of applying the first-order expression to describe a reaction must be checked by examining [A] as a function of time. A reaction that follows first-order kinetics will yield a plot of eq 5 in which the data fall on a straight line. Recall also that the half-life of the reaction is commonly expressed as the time required for half of the initial quantity of A to decompose and is defined as

$$t_{1/2} = \ln 2/k = 0.693/k \quad (6)$$

where *t*_{1/2} is the half-life. In the case where the rate constant is determined from the increase in products using eq 3, the half-life is more accurately described as the time interval required for the quantity of products to increase by a factor of 2. For a first-order reaction, the half-life is independent of the concentration and the first and subsequent half-lives should be the same. Note that this is not the case for reaction orders other than 1, where, like the rate constant, *t*_{1/2} will show some concentration dependence.

In the context of the measurements presented here, *t*_{1/2} has great practical utility. This value is more informative than a rate constant in the design of property measurement protocols. Thus, a *PVT* or transport property measurement will take a given time to

accomplish, and with $t_{1/2}$, this can be related to the time for the concentration of thermal decomposition products to increase to an unacceptable level.

In addition to reaction rate constants, the rate constant determined at various temperatures can be used to calculate predictive parameters in the Arrhenius expression

$$k = A \exp(E_a/T) \quad (7)$$

where A is the preexponential factor, E_a is the activation energy, and T is the temperature. These Arrhenius parameters can be used to predict the rate constant at temperatures other than those examined experimentally.

Experimental Section

Chemicals. Reagent-grade *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, toluene, acetone, and methanol were obtained from commercial suppliers. All materials were analyzed by GC and found to be of acceptable purity and were therefore used as received. Two samples of RP-1 were supplied by the Aero Propulsion and Power Directorate at Wright Patterson Air Force Base. The first sample was unusual in that chemical analysis showed a much larger fraction of olefinic and aromatic compounds than would be expected in a typical kerosene fraction. Approximately 20% of the compounds identified in this mixture had a double bond or an aromatic ring. It is therefore representative of an off-specification RP-1. The second sample was more typical of a kerosene rocket propellant, with very low olefinic and aromatic fractions. Both of these samples, which were pale pink in color (because of the presence of an added dye, azobenzene-4-azo-2-naphthol), were used as received. Detailed chemical analyses [by gas chromatography (GC), mass spectrometry (MS), and infrared spectrophotometry (IR)] of these fluids were done as part of this work, and this is available elsewhere.²⁰ In addition to analysis by GC, MS, and IR, a total sulfur analysis was done by GC with a sulfur chemiluminescence detector (SCD), and a copper strip corrosion test (CSCT) was also done. The results of the SCD and CSCT indicated that both the off-specification sample and the typical sample were very low in sulfur. The results from the GC and SCD measurements showed that the sulfur peaks were nearly at the detection limit of the instrument/method, at 100 ppb (mol/mol). Exposed copper strips that were indistinguishable from pristine strips were recovered from the CSCT.

Apparatus. The simple apparatus assembled to make the decomposition kinetics measurements is shown in Figure 1. The apparatus consisted of a 304 (AISI designation) stainless steel thermal block that is heated to the desired experimental temperature. In the work reported here, temperatures between 375 and 500 °C were used. Stainless steel was chosen for the block because of its favorable mechanical and corrosion properties at high temperature. The block was supported in an insulated box with carbon rods, which were chosen for low thermal conductivity. The temperature was maintained and controlled (by a proportional–integral–derivative controller) to within ± 0.1 °C in response to a platinum resistance sensor embedded in the thermal block and sealed with ceramic adhesive. The cells consisted of a 6.4 cm length of ultrahigh-pressure 316

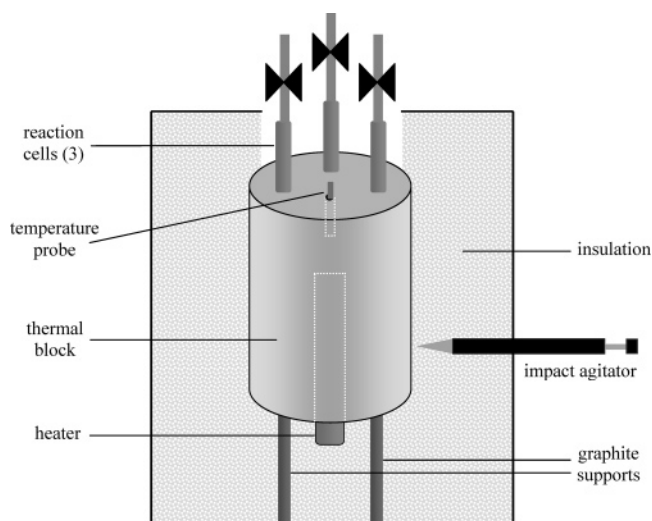


Figure 1. Apparatus used to thermally stress and decompose RP-1.

stainless steel tubing (0.64 cm external diameter and 0.18 cm internal diameter) that was sealed on one end with a stainless steel plug welded by a clean tungsten inert gas (TIG) process. Each cell was connected to a high-pressure valve at the other end with a short length of 0.16-cm-outer-diameter 316 stainless steel tubing with an internal diameter of 0.02 cm. This length of tubing was also TIG-welded to the cell. The valves were appropriate for high temperature in that the seats were stainless steel and the packings were polyimide. Each cell and valve was capable of withstanding a pressure in excess of 105 MPa at the desired temperature. Although not used in the experiments described here, an impact agitator was attached to the heating block for use when heterogeneous systems are investigated.

The internal volume of each cell (including the short length of the connecting tubing and the small dead volume of the valve) was determined by gravimetric gasometry using liquid carbon dioxide. This procedure consisted of filling a cell of known mass with carbon dioxide to a predetermined pressure (20.68 MPa) and at a constant temperature. The cell mass was measured again, and the increase in mass allowed the calculation of the cell volume by use of a precise equation of state for the density of carbon dioxide.²¹ Cell volumes were measured three times and averaged to yield 0.210 ± 0.002 , 0.226 ± 0.001 , and 0.235 ± 0.003 cm³ for the three vessels.

The cell-filling procedure was a critical step because we desired to mimic the conditions that might be encountered in our physical property measurement apparatus. We modified a computer program that provides the necessary fluid mass to achieve a selected pressure at the desired temperature.²² This program allowed us to determine the target mass to place in the evacuated cell, given the cell volume, to achieve a nominal 34.5 MPa at temperatures between 375 and 500 °C. An equation of state for *n*-dodecane was used to estimate the pressure in each cell at the decomposition temperature.²² Although RP-1 is composed of many compounds, models derived from the properties of *n*-dodecane have been successfully used to model the physical properties of kerosene fuels.^{23,24}

The calculated mass of RP-1 was added to the cell with a syringe equipped with an ultrafine needle, and the mass of the cell was measured to within ± 0.0001 g.

The valve was then affixed to the cell and sealed. Sample masses were typically on the order of 0.1 g and varied depending on the experimental temperature and cell volume. Cells were then chilled to $-196\text{ }^{\circ}\text{C}$ in liquid nitrogen and subsequently evacuated to 10 Pa through the valve to remove air from the cell. The valve was then closed, and the cell was warmed to room temperature, at which time the mass of the entire cell–valve assembly was recorded.

Loaded cells were then inserted into a stainless steel thermal block that was heated to the desired experimental temperature. Fluid reflux inside the cells was minimized by ensuring that the entire length of the cell, transfer line, and most of the valve were located in the hot zone. The cells were maintained at the reaction temperature for a specified period of time ranging from 4 min to 20 h. After the desired time period, the cells were removed from the thermal block and quenched in water at room temperature. The cells were dried, and the mass was measured to ensure that no leakage had occurred over the course of the experiment. The thermally stressed RP-1 was then recovered from the cells and analyzed.

After each run, the cells and valves were solvent-rinsed with hexanes, toluene, acetone, and finally methanol with an ultrafine needle. Solvent rinsing was performed until each solvent was colorless as it exited the cell. Cleaned cells and valves were heated to $150\text{ }^{\circ}\text{C}$ for at least 30 min to remove residual solvent.

A blank experiment was performed to investigate any possible artifacts introduced in the experiment such as residual solvent in the cell or possible catalytic behavior of the cell materials. The cells were loaded and evacuated as described above and then maintained at room temperature for 65 h. The liquid sample was then removed and analyzed in the same manner as that of the samples that had been exposed to elevated temperature.

Analytical Method. The purpose of the analytical procedure described here was to measure the decomposition kinetics of the thermally stressed RP-1. As such, a detailed identification of each product is unnecessary; only the rate of composition change is required. We point out, however, that a detailed analysis of RP-1 and its decomposition products has been done as part of this project and is reported elsewhere.²⁰ A liquid sampling procedure was developed to minimize sample loss when the cells were opened. A short length of stainless steel tubing was connected to the valve outlet and placed inside a prechilled (at $7\text{ }^{\circ}\text{C}$) glass vial. The valve was slowly opened, and the reacted RP-1 was expelled and collected in the vial. The cell was then removed from the valve, and any sample remaining in the cell was transferred to the glass vial using a syringe equipped with an ultrafine needle. Samples were refrigerated (at $7\text{ }^{\circ}\text{C}$) until the analysis was performed. Liquid samples were prepared for GC analysis by dilution in *n*-dodecane. The resulting solution was typically 8% reacted RP-1 (mass/mass). The uncertainty in the mass measurement was $\pm 0.0001\text{ g}$. Sample vials were crimp-sealed, and the contents were mixed with a vortex mixer.

Aliquots ($2\text{ }\mu\text{L}$) of the sample were injected into a gas chromatograph equipped with an automatic sampler and a flame ionization detector. Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was maintained at $300\text{ }^{\circ}\text{C}$, and

samples were separated on a capillary column (30 m column coated with a $1\text{ }\mu\text{m}$ film of 100% dimethylpolysiloxane). A temperature program was used that consisted of an initial isothermal separation at $100\text{ }^{\circ}\text{C}$ for 2 min, followed by a $7\text{ }^{\circ}\text{C}/\text{min}$ gradient to $225\text{ }^{\circ}\text{C}$. This final temperature was held constant for 15 min.

Chromatographic analysis was performed on a suite of emergent decomposition peaks. These were peaks corresponding to products formed during the thermal stress; they were not present in the unreacted RP-1. For the measurements done at 375, 400, and $425\text{ }^{\circ}\text{C}$, the same product suite was used to determine decomposition kinetics for both samples. The emergent product suite at $500\text{ }^{\circ}\text{C}$ was found to be very different from that observed at the three lower temperatures, and therefore, at this temperature, a different product suite was used. Retention times from a standard solution of *n*-alkanes were used to account for the day-to-day variations in the retention times of the decomposition products. This was done with a mixture of *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane that was analyzed before and after each RP-1 sample. Retention times of the reference alkanes were used to bracket and predict the retention times of the major decomposition products and were remarkably consistent throughout this study. A linear regression was used to fit the data and typically yielded correlation coefficients greater than 0.99999, and predicted retention times were typically within $\pm 0.01\text{ min}$ of the measured product retention times. This procedure ensured that no extraneous peaks were used in the chemical analyses upon which the reaction kinetics were based.

RP-1 decomposition was observed from the increase in the chromatographic signal of the degradation products. Chromatograms of unreacted RP-1 exhibited no peaks below a retention time of 8 min, whereas the degradation products were observed to elute earlier than 8 min. Several decomposition peaks were included in the determination of the rate constant (seven peaks at 375, 400, and $425\text{ }^{\circ}\text{C}$ and three peaks at $500\text{ }^{\circ}\text{C}$). These peaks were selected on the basis of chromatographic considerations: near-baseline resolution, good peak shape (absence of shoulders or tailing), and the magnitude of their peak area. These factors served to minimize the uncertainty in the integrated areas obtained from a chromatogram.

Vapor-Phase Decomposition Products. While the global decomposition rate constants reported here were determined exclusively from decomposition products found in the thermally stressed liquid fuel, a vapor phase was generated in most of the experiments. This vapor phase had a significant pressure, although on a molar basis, we estimate that the vapor was, overall, a very small fraction of the total product suite. Indeed, it was the pressure of the vapor that expelled most of the liquid sample from the cells after each decomposition measurement. We therefore investigated the vapor phase as part of this decomposition study. The desire here was to obtain some understanding of the composition and pressure of the vapor phase.

To obtain a chemical analysis of the vapor phase, we used the gas–liquid separator, designed and built for this work, shown in Figure 2.²⁵ This device, which is similar in concept to branch-point separators in natural gas transmission lines,²⁶ was constructed from a 316 stainless steel tube T fitting. Branch-point separators have demonstrated effectiveness due to the volume

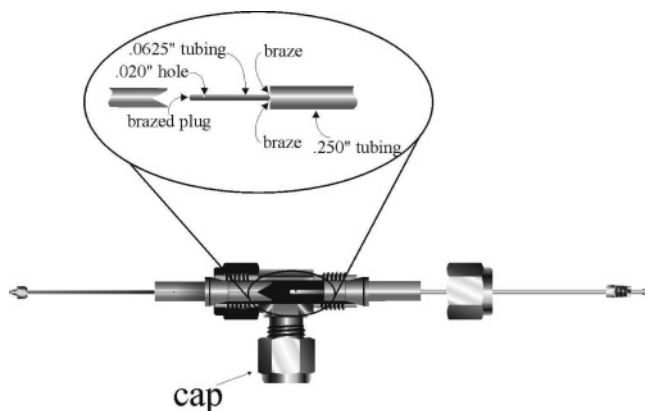


Figure 2. Gas-liquid separation device.

Table 1. RP-1 Decomposition Kinetics Parameters

T (°C)	$k \pm 1\sigma$ (s ⁻¹)	$t_{1/2}$ (min)	$k \pm 1\sigma$ (s ⁻¹)	$t_{1/2}$ (min)
	RP-1, high olefin		RP-1, within specification	
375	$(6.92 \pm 0.75) \times 10^{-5}$	167	$(1.13 \pm 0.04) \times 10^{-5}$	1022
400	$(2.00 \pm 0.23) \times 10^{-4}$	58	$(1.19 \pm 0.33) \times 10^{-4}$	97
425	$(3.85 \pm 0.53) \times 10^{-4}$	30	$(3.08 \pm 0.77) \times 10^{-4}$	38
500	$(1.07 \pm 0.17) \times 10^{-3}$	11		

Table 2. Summary of RP-1 Reaction Products Found in the Vapor Phase after Thermal Stress at 450 °C for 66 min

compound name	mass %	compound name	mass %
propane	46.7	benzene	3.7
2-methylbutane	24.9	1,3-dimethylcyclopentane	1.4
2-methylpentane	7.8	<i>n</i> -heptane	1.8
<i>n</i> -hexane	7.7	methylcyclohexane	1.4
methylcyclopentane	3.4	toluene	1.2

change encountered in the enclosure of the separator and due to the position of the vapor collection tube. Similarly, the device shown in Figure 2 effectively strips off the liquid phase from the vapor, allowing an independent chemical analysis of the vapor. Analysis of the vapor phase was performed using a gas chromatograph with MS detection. Vapor was introduced directly into the split/splitless injection port of the chromatograph and was separated on a capillary column (30 m column coated with a 0.25 μm film of 5% phenylmethylpolysiloxane). A temperature program was used to separate the sample with an initial isothermal separation at 60 °C for 2 min, followed by a 2 °C/min ramp to 90 °C and then followed by a 10 °C/min ramp to 250 °C. MS spectra were recorded for fragments of relative molecular mass from 20 to 350. A listing of the compounds observed is provided in Table 2. Note that the MS method employed would preclude observation of single-carbon species.

We also measured the residual pressure that was present in our experimental cells after a reaction had been quenched to ambient temperature. This was done by installing a manifold with a Bourdon tube pressure gauge to the reaction cell through the valve. With this arrangement, we were able to determine the residual pressure at ambient temperature only, after the reaction had been quenched to ambient temperature. It was not possible to make a similar measurement at the high temperatures of the decomposition measurements because of the potential of fluid reflux in the pressure gauge. The residual pressure measured ranged from a low of slightly above ambient pressure (that is, a barely

discernible change on the gauge) for an exposure at 375 °C to 6.7 MPa (970 psia) after measurements at 500 °C.

Results and Discussion

As stated earlier, samples from two independent lots of RP-1 were available for measurement: one with a relatively high olefin content and one that was more typical of a kerosene. For each of the two samples, decomposition kinetics measurements were made at 375, 400, and 425 °C. In addition, for the high-olefin RP-1, measurements were also made at 500 °C. At this temperature, the reaction was very fast and represents the capability limit of our simple apparatus. Measurements at this temperature were difficult in that ampules had to be heated to the reaction temperature individually, not three ampules simultaneously, as could be done for all of the lower temperatures. No measurements could be made above this temperature because the equilibration time approached the reaction time. We also attempted measurements at 325 °C; however, no decomposition products were observed after 60 min, and after 67 h, only a few decomposition products with chromatographic retention times of less than 4 min were observed. Thus, our practical window of measurement was limited to between 375 and 425 °C.

Qualitatively, thermal stress of both RP-1 samples produced rapid visual changes, even at the lowest temperatures measured in these studies. The pink dye present in both samples (azobenzene-4-azo-2-naphthol) reacted very quickly because, even after a brief exposure to elevated temperature, the liquids became colorless. Then, as exposure times increased, the clear liquid would gradually take on a yellow, then an orange, and finally a brown color. Only the samples run at 500 °C were observed to produce particulates, but particulate production at this temperature was observed at exposure times as short as 4 min.

In the chromatographic analysis of the thermally stressed fluids, most of the emergent products had retention times that were much shorter than those of the unreacted components. In fact, the product suite consistently emerged as a separate band of peaks preceding the typical broad kerosene "hump". We noted a few decomposition peaks that could be ascribed to heavier components; however, none of these were used in the measurements. While there undoubtedly were decomposition peaks that developed in the kerosene hump, using them was impractical because of overlap and the frequent lack of baseline resolution. This suggests that most of the RP-1 decomposition produced smaller fragments rather than larger polymeric species. The product suite that was observed at 375, 400, and 425 °C was essentially the same, with retention times that were constant to within ± 0.01 min. At 500 °C, the product suite changed and different retention times were observed for the emergent products. This is consistent with our detailed analytical results in which numerous naphthalenic compounds were observed to form at this temperature but not at the lower temperatures.²⁰ The reaction rate constants presented here were derived from measurements of liquid decomposition products only. Products that were not retained in the decomposed RP-1 liquid were not monitored, including vapor-phase products and potential coke deposits.

For all of our measurements on both RP-1 samples, plots of \ln [products] as a function of time showed a linear portion that persisted for an appreciable time,

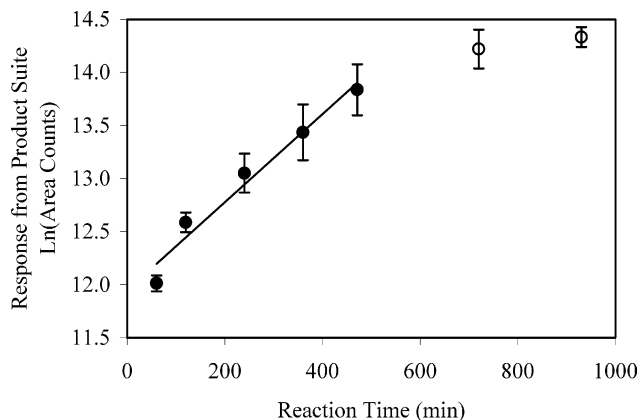


Figure 3. First-order plot for high-olefin RP-1 decomposition at 375 °C. Only the data at short reaction times (solid circles) were fitted to a linear regression and included in the determination of the rate constant.

followed by a curved area and finally a leveling off of the curvature. The deviation from linearity at higher reaction times is likely due to the onset of subsequent reactions that affect the concentration of the initial products, corresponding to ΣB_i . For practical applications in predicting the behavior of this fluid (in motors and in measurement apparatuses), it is valid to use the linear portion of the trends to determine a global pseudo-first-order rate constant. By this, we mean that it is very unlikely that measurements would intentionally be carried out with instrumental residence times in excess of the time represented by the linear portion of the plot. This area of the plot is, nevertheless, useful in that it represents the chemical decomposition regime that is possible if an instrument or motor enters an upset condition in which the residence time is longer than optimal.

An example of such a plot is shown in Figure 3, in which data for 375 °C are presented. The decomposition rate constants for both fluids, at all of the temperatures measured, are presented in Table 1. Each rate constant was calculated with data collected from at least four reaction times, where decomposition measurements were run in triplicate for each reaction time. Uncertainties were calculated from the standard deviation for each triplicate of measurements and from the standard error in the slope of the regression. The value presented as $t_{1/2}$ is actually the time required for the impurity concentration to double, as was explained in the Theory section. The temperature dependence of the decomposition reaction for the high-olefin RP-1 is shown in Figure 4. The data yield an Arrhenius expression equal to $k = 980 \text{ s}^{-1} \exp[-1.05 \times 10^4/T \text{ (K)}]$ with an activation energy of $87 \pm 15 \text{ kJ/mol}$. Note that this is considerably lower than the value measured for pure dodecane: $E_a = 260 \text{ kJ/mol}$.²⁷ It is clear from this difference, and from the difference in the rate constants in Table 1, that the higher olefin content of this sample results in a much lower thermal stability. An Arrhenius plot was not done for the typical RP-1 composition because data were measured at only three temperatures.

Conclusions

The thermal decomposition of two samples of RP-1 was measured with a static ampule method. This was done primarily to guide our measurements of the thermophysical properties of these fluids at high tem-

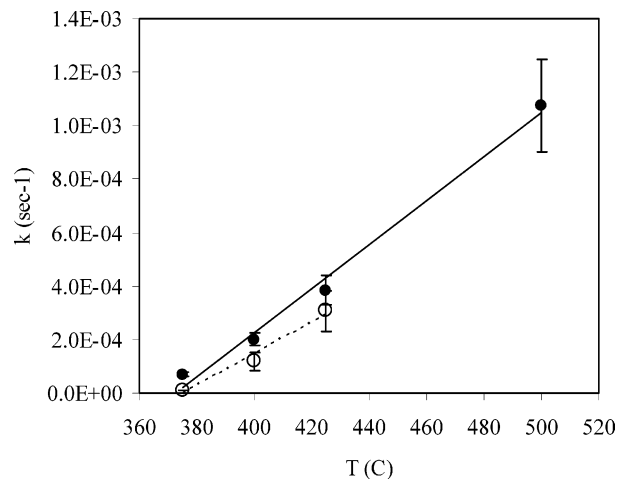


Figure 4. Temperature dependence of the high-olefin RP-1 decomposition from 375 to 500 °C (filled circles) and the more typical RP-1 from 375 to 425 °C (open circles).

peratures. We can conclude that the thermal decomposition becomes a serious issue for thermophysical property measurements at temperatures above 400 °C. Below this temperature, the fluid is stable enough for measurements that require residence times on the order of a few hours. Above 400 °C, the decomposition is relatively rapid and will prevent residence times of more than a few minutes. At temperatures near 500 °C, measurements must be made with residence times on the order of 2–3 min to avoid serious decomposition products from interfering.

Acknowledgment

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