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Thermal Decomposition Kinetics of Propylcyclohexane

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As part of a large-scale thermophysical property measurement project, the decomposition kinetics of propylcyclohexane was investigated. Decomposition reactions were performed at 375, 400, 425, and 450 °C in stainless steel ampule reactors. At each temperature, the extent of decomposition was determined as a function of time by gas chromatography. These data were used to derive first-order rate constants for the decomposition of propylcyclohexane. Decomposition rate constants ranged from $3.66 \times 10^{-7}$ s$^{-1}$ at 375 °C to $8.63 \times 10^{-5}$ s$^{-1}$ at 450 °C. Among other things, these rate constants are useful for planning property measurements at high temperatures. Based on the amount of time required for 1% of the sample to decompose ($t_{0.01}$), we found that allowable instrument residence times ranged from about 8 h at 375 °C to about 2 min at 450 °C. The kinetic data were also used to determine Arrhenius parameters of $A = 2.56 \times 10^{16}$ s$^{-1}$ and $E_a = 283$ kJ·mol$^{-1}$. In addition to the decomposition kinetics, we have also done a GC–MS analysis in order to identify the most abundant decomposition products.

Introduction

Kerosene-based fuels are of great importance for military and aerospace applications.$^{1-4}$ Such fuels are complex mixtures of hydrocarbons with hundreds or even thousands of constituents.$^{5-7}$ Each type of kerosene fuel must meet certain physical property specifications, but substantial compositional variation is possible.$^{2,5-7}$ Because of their complexity, the compositions of kerosene-based fuels are often reported in terms of chemical classes (e.g., linear alkanes, aromatics) instead of individual compounds (e.g., dodecane, hexylobenzene). Cycloalkanes, like propylcyclohexane, which are also called naphthenes or cycloparaffins, are an important class of chemicals in many kerosene fuels.$^{2,5-8}$

A large-scale project involving the thermophysical properties of kerosene-based fuels is in progress at the National Institute of Standards and Technology (NIST). One aspect of this project involves the measurement of thermophysical properties of kerosene-based fuels.$^{9-14}$ This is followed by the development of equations of state to correlate the property data.$^{9,11,14}$ Such work enhances design and operational specifications of these fluids and facilitates new applications.

Another part of the project on kerosene-based fuels involves the development of fuel models based on “surrogate” mixtures. The complexity and compositional variability of “real” kerosene fuels can be an obstacle to fundamental research and modeling.$^{5,6}$ For this reason, the development of simple mixtures (surrogates) that closely approximate the behavior of real fuels is critical.$^{6,13,15}$ Such surrogate mixtures might contain only a dozen or fewer components. Mixture components are typically chosen to represent classes of chemicals in the fuel being modeled. Following this line of thought, propylcyclohexane has been chosen for several reasons as a representative cycloalkane in the surrogate fuel mixtures being developed at NIST.$^{15,16}$

The inclusion of propylcyclohexane in surrogate fuel mixtures required a complete fluid model for this compound, thus requiring that its thermophysical properties be measured over a wide range of temperatures and pressures. This includes temperatures greater than 300 °C and pressures greater than 10 MPa, areas in which data are scarce.$^{7}$ Under these conditions decomposition is a serious concern because it can affect the validity of the data that are obtained and the performance, lifetime, and safety of the instruments used to collect the data. Obviously, the extent of decomposition that occurs during thermal equilibration and property measurement has a direct impact on data quality. Additionally, decomposition of hydrocarbons can lead to the formation of solid deposits$^{18-21}$ that may affect instrument performance and that are often difficult to remove. Changes in composition can also result in catastrophic increases in pressure. Recent work on kerosene-based fuels clearly validates such concerns for property measurements at high temperature and pressure.$^{22-26}$ In order to avoid problems with decomposition during property measurements, one must understand the kinetics of decomposition.

Herein we report the results of a study of the kinetics of thermal decomposition for propylcyclohexane. First-order rate constants for the thermal decomposition of propylcyclohexane were determined from 375 to 450 °C by use of a method that we previously developed for the kerosene-based fuels and a series of organic Rankine cycle fluids.$^{22,26,27}$ That is, the fluid was thermally stressed in ampule reactors made of 316L stainless steel, and the extent of decomposition was determined as a function of time by gas chromatography. The Arrhenius parameters for thermal decomposition were determined from a plot of the rate constants as a function of the temperature.$^{22,27-31}$ The Arrhenius parameters are especially useful because they can be used to predict decomposition rates at temperatures other than those determined experimentally. The initial motivation for this work was to establish operating ranges for thermophysical property measurements on propylcyclohexane, but the results clearly have value for modeling and engineering studies as well.

Experimental

Chemicals. Reagent-grade acetone, toluene, and dodecane were obtained from commercial sources. All had purities of no less than 99% and were used as received. Propylcyclohexane was obtained from Aldrich and used as received. It had a stated purity of 99%, which is consistent with our own GC analyses of unheated samples of the propylcyclohexane (e.g., see the top

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chromatogram in Figure 2). The commercial source of the propylcyclohexane is provided as an important scientific detail, but this does imply an endorsement of the product by the National Institute of Standards and Technology; other products could perform equally well or better.

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 in the center of an insulated box on carbon rods, which were chosen for their low thermal conductivity. 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 ampule reactors could be placed into tight-fitting holes in each of the thermostatted blocks. Each ampule 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 (0.64 cm external diameter and 0.16 cm internal diameter) 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 (0.16 cm external diameter and 0.08 cm internal diameter) 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 in excess of 100 MPa at the temperatures used. The internal volume of each cell, including the short length of narrow connecting tubing, but not including the relatively small noxious volume (i.e., swept dead volume) of the valve, was determined gravimetrically from the mass of toluene required to fill it. Each cell volume was determined two or three times, and the average value (typically about 0.11 mL) was used for subsequent calculations.

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 about 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 not done in a particular 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 in this system.

Decomposition Reactions. The procedure used to fill the ampule reactors was designed to achieve an initial target pressure of 34.5 MPa (5000 psi) for all decomposition reactions. 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 propylcyclohexane, a computer program calculated the mass of propylcyclohexane needed to achieve a pressure of 34.5 MPa at a given temperature and cell volume. The calculated mass of propylcyclohexane was added to the cell with a syringe equipped with a 26 gauge needle (sample masses were typically on the order of 0.06 g and varied depending on the experimental temperature and 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 reclosed, and the cell was warmed to room temperature. More rigorous degassing of the liquid is not necessary because the autoxidation reactions caused by traces of dissolved oxygen are relatively unimportant for hydrocarbon decomposition above 250–300 °C.

The loaded ampule 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 ampule reactor inside the thermostatted block). The ampule reactors were maintained at the reaction temperature for a specified period ranging from 10 min to 32 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 was shorter than 30 min. After decomposition, the reactors were removed from the thermostatted block and immediately cooled in room-temperature water. The thermally stressed propylcyclohexane 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 about 5 min (while filled with the acetone/toluene 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 propylcyclohexane as described above, but the cell was not heated above room temperature. After about a day, the propylcyclohexane 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 propylcyclohexane, and by the absence of decomposition products in the resulting gas chromatogram (for example, see the top chromatogram in Figure 2).

Analysis of Liquid-Phase Decomposition Products by Gas Chromatography (GC). The production of light decomposition products caused the pressure in the ampule reactors to increase during the decomposition reactions. After decomposition, the ampule reactors contained a pressurized mixture of vapor and liquid, even at room temperature. Liquid-phase decomposition products in the thermally stressed propylcyclohexane were used to monitor the kinetics of decomposition. Therefore, a sampling procedure was designed to minimize loss of the liquid sample when the ampule reactors were opened. Specifically, a short length of stainless steel tubing was connected to the 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 propylcyclohexane 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 with a 26 gauge needle. 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 immediately diluted with a known amount of n-dodecane and refrigerated (at 7 °C) until the analysis was performed. The purpose of this procedure was to prepare the samples for GC analysis and to minimize evaporative losses from the samples. The resulting n-dodecane solution was typically 5% reacted propylcyclohexane (mass/mass).

Aliquots (3 µL) from crimp-sealed vials of each 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 °C, and samples were separated on a 30 m capillary column coated with a 0.1 µm film of (5%-phenyl)methylpolysiloxane. A temperature program was used that consisted of an initial isothermal separation at 80 °C for 4 min, followed by a 30 °C/min gradient to 250 °C. This final temperature was held constant for 1 min.

Propylcyclohexane decomposition was observed from the relative decrease in the chromatographic signal of propylcyclohexane compared to the chromatographic signals for decomposition products. The fraction of undecomposed propylcyclohexane was calculated by dividing the propylcyclohexane peak area by the total peak area (excluding peaks due to the dodecane solvent). This simple use of area percent for the kinetic analysis is possible only because of the types of compounds being analyzed and the use of a flame ionization detector. For alkanes and alkenes, the relative sensitivity of the detector (based on moles of carbon) varies by only a few percent. Consequently, calibrating the detector for each individual compound is not expected to significantly change the derived rate constants. At 450 °C, the longest decomposition time was 40 min, at which point about 20% of the propylcyclohexane had decomposed. At 425 °C, the longest decomposition time was 3 h, at which point about 15% of the propylcyclohexane had decomposed. At 400 °C, the longest decomposition time was 6 h, at which point about 5% of the propylcyclohexane had decomposed. At 375 °C, the longest decomposition time was 32 h, at which point about 5% of the propylcyclohexane had decomposed.

Identification of the Decomposition Products by Gas Chromatography−Mass Spectrometry (GC−MS). The products of a 40 min decomposition reaction at 450 °C were identified by GC−MS. To accomplish this, a short length of glass capillary tubing was connected to the outlet on the reactor valve. The end of the capillary was submerged in a vial of water. Then the valve on the reactor was opened just enough to allow the pressurized mixture of gas and liquid in the cell to escape slowly, causing bubbles to form at the end of the submerged capillary. After the observation of bubbling, the end of the capillary was removed from the vial of water and briefly pushed through the inlet septum of the split/splitless injection port of the GC−MS, directly introducing the decomposed sample by flowing capillary injection. The components of the sample were then separated on a 30 m capillary column coated with a 0.25 µm film of (5%-phenyl)methylpolysiloxane. The temperature program for the separation started with an initial isothermal separation at 35 °C for 6 min, followed by a 20 °C/min ramp to 175 °C. MS spectra were recorded for fragments of relative molecular mass from 14 to 550.

Results and Discussion

Aliquots of propylcyclohexane were thermally stressed in sealed stainless steel ampule reactors with an initial pressure of 34.5 MPa (5000 psi) and temperatures of 375, 400, 425, and 450 °C. These conditions mimic the high-pressure conditions that existed during some of our physical property measurements. This temperature range was chosen because it allowed for reaction times of a convenient length. At 375 °C, the reaction is relatively slow, so reaction times ranged from 16 to 32 h. At 450 °C, the reaction is much faster, so reaction times ranged from 10 to 40 min.

The unreacted propylcyclohexane was clear and colorless. Even after the longest reaction times at the higher temperatures, the liquid remained clear and colorless (although a very small amount of dark particulate was regularly seen in the most thermally stressed samples). This contrasts with the behavior of kerosene fuels, which become dark brown and opaque when submitted to this kind of thermal stress. During the decomposition of propylcyclohexane, low-molecular-weight decomposition products caused a pressurized vapor phase to
develop inside the reactors. For the most severely stressed samples, it was common for about half of the liquid sample to be expelled under pressure when the reactor valve was opened.

Using GC–MS, we identified the products of a 40 min decomposition reaction at 450 °C. Table 1 shows the 14 most abundant compounds, based on total ion current in the MS detector. A thorough analysis of the thermal decomposition products of propylcyclohexane has been reported previously. In that work, propylcyclohexane was decomposed in a stainless steel reactor at 450 °C, and decomposition products were monitored as a function of time for up to 4 h. The primary difference between our decomposition reactions and those of the previous work is that we used a considerably higher initial pressure (34.5 MPa compared to about 4 MPa). Higher pressure is known to affect the ratio of products of alkane decompositions; for example, it can result in lower yields of primary alkanes. For the most severely stressed conditions; for example, it can result in lower yields of primary alkanes. For the most severely stressed conditions; for example, it can result in lower yields of primary alkanes. For the most severely stressed decompositions; for example, it can result in lower yields of primary alkanes. For the most severely stressed decompositions; for example, it can result in lower yields of primary alkanes. For the most severely stressed decompositions; for example, it can result in lower yields of primary alkanes. For the most severely stressed decompositions; for example, it can result in lower yields of primary alkanes.

Nevertheless, with the exception of propene and methane, the most abundant decomposition products observed previously are the same ones we observed (Table 1). The thermally stressed liquid phase of every decomposition reaction was analyzed by gas chromatography equipped with a flame ionization detector (GC–FID). We did not routinely monitor compounds that were not retained in the liquid phase, including vapor-phase products and potential coke deposits. Figure 2 shows the suite of decomposition products that was seen in the GC–FID chromatograms. All of the larger product peaks had retention times shorter than that of propylcyclohexane. The decomposition products observed were essentially the same at all temperatures, although there were minor changes in the relative abundances of products at different temperatures. We did not attempt to identify the individual peaks by retention time, but the product suite observed by GC–FID appears consistent with the product suite identified by GC–MS. These routine GC–FID analyses allowed us to track the extent of decomposition for each reaction. For example, about 20% of the propylcyclohexane had decomposed after 40 min at 450 °C, but only about 5% of the propylcyclohexane had decomposed after 32 h at 375 °C.

The kinetic analysis was done by monitoring the loss of propylcyclohexane as a function of time, t, during the decomposition reactions. At each temperature, data were collected at four or five different reaction times, with 3–5 replicate decomposition reactions run at each reaction time. Rate constants, k, for decomposition were obtained by fitting these data to a first-order rate law, eqs 1–3. The half-life, t_0.5, at each temperature (i.e., the time required for one-half of the propylcyclohexane to decompose) was then calculated from the rate constant using eq 4. A related quantity is the time it takes for 1% of the reactants to become products, t_0.01. For first-order reactions, t_0.01 is calculated from the rate constant using eq 5. Finally, the rate constants for decomposition were used to evaluate the parameters of the Arrhenius equation, eq 6.

\[
A \rightarrow B \quad (1)
\]
\[
-d[A]/dt = d[B]/dt = k \quad (2)
\]
\[
\ln[A] = \ln[A]_0 - kt \quad (3)
\]
\[
t_{0.5} = 0.6931/k \quad (4)
\]
\[
t_{0.01} = 0.01005/k \quad (5)
\]
\[
k = A \exp(-E/R\theta) \quad (6)
\]

The data for the decomposition reactions at 450 °C are shown in Figure 3. The value of k at 450 °C, obtained from the slope of the linear fit in Figure 3, is 8.63 × 10^{-5} s^{-1} with a standard uncertainty of 0.18 × 10^{-5} s^{-1}. Values for t_{0.5} and t_{0.01} were calculated from k using eqs 4 and 5. The decomposition rate constants at all four temperatures, along with values of t_{0.5} and t_{0.01}, are presented in Table 2. The standard uncertainties given in Table 2 were calculated from the standard deviation of replicate measurements and from the standard error in the linear fit. The values of t_{0.01} show that apparatus residence times of several hours may be acceptable for property measurements at 375 °C. On the other hand, at 450 °C residence times longer than a couple of minutes may be unacceptable.

It is noteworthy that all three data points for the 10 min decompositions at 450 °C are above the linear fit (Figure 3); more specifically, the amount of observed decomposition for these points is about 20% less than the fit predicts. We believe that the explanation for this phenomenon is that the thermal equilibration time for these reactions is a significant fraction of the overall reaction time. In fact, the position of the 10 min...
data points relative to the fit line can be used to deduce an effective thermal equilibration time of about 2 min. This behavior was not observed at lower temperatures, where the shortest decomposition reactions were 30 min or longer.

An Arrhenius plot of the rate constants is shown in Figure 4. The Arrhenius parameters determined from a linear regression of the data are \( A = 2.56 \times 10^{16} \) s\(^{-1}\) and \( E_a = 283 \) kJ mol\(^{-1}\). The standard uncertainty in \( E_a \), calculated from the standard error in the slope of the regression, is 6 kJ mol\(^{-1}\). The Arrhenius plot is notably linear \( (r^2 > 0.99) \) over the 75 °C temperature range of these experiments.

Previously existing data\(^{36,38,39}\) for the kinetics of propylcyclclohexane decomposition were all obtained at pressures of about 4 MPa or less. This compares complication of our data with existing data because the effect of pressure on the decomposition kinetics of hydrocarbons appears to be complex and compound-dependent.\(^{27,38,40}\) In fact, a substantial pressure effect has been observed\(^{38}\) for the decomposition of \( r \)-butylcyclclohexane (the rate constant doubled in going from about 3 MPa to about 6 MPa), so it is reasonable to expect a pressure effect for the decomposition of propylcyclclohexane. With this in mind, we will review the literature data for the kinetics of propylcyclclohexane decomposition. A rate constant of \( 6.9 \times 10^{-5} \) s\(^{-1}\) (no uncertainty was given) has been reported for propylcyclclohexane decomposition at 450 °C and \( \sim 4 \) MPa in a stainless steel reactor,\(^{36}\) which is about 20% lower than our value at 450 °C. In another report, an average rate constant of \( 2.34 \times 10^{-5} \) s\(^{-1}\) (with a standard deviation of 10.1%) was reported for propylcyclclohexane decomposition at 427 °C and \( 4 \) MPa in a glass reactor.\(^{38}\) Using the Arrhenius parameters from the previous paragraph, we predict a value of \( 1.95 \times 10^{-5} \) s\(^{-1}\) at this temperature, which is about 17% lower than the literature value. In a third report,\(^{39}\) the decomposition of propylcyclclohexane was studied in a metallic flow reactor at atmospheric pressure and temperatures from 660 to 800 °C. Under these conditions, Arrhenius parameters of \( A = 8.8 \times 10^{12} \) s\(^{-1}\) and \( E_a = (241 \pm 2) \) kJ mol\(^{-1}\) were obtained,\(^{39}\) which are much lower than the values obtained in our experiments. Activation energies for some other alkylcyclclohexanes have been reported.\(^{36,41}\) They were determined by using approximately the same temperature range that we used, but lower pressure (\( \sim 4 \) MPa). Under these conditions the activation energies center around 260 kJ mol\(^{-1}\), which is about halfway between the value at atmospheric pressure and our value at 34.5 MPa.

The thermal decomposition of propylcyclclohexane is more complex than the reaction shown in eq 1 because it can decompose by more than one reaction pathway, the decomposi-

**Figure 4.** Arrhenius plot for the decomposition of propylcyclclohexane. No error bars are shown because the uncertainties in the values of \( \ln k \) are smaller than the symbols. The Arrhenius parameters determined from the fit to the data are \( A = 2.56 \times 10^{16} \) s\(^{-1}\) and \( E_a = 283 \) kJ mol\(^{-1}\).


