Thermal Decomposition Kinetics of 1,3,5-Triisopropylcyclohexane

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ABSTRACT: Recent surrogate diesel fuel mixture development identified the need for a multiply substituted, low cetane number, high molecular mass monocycloalkane component. On the basis of a thermophysical property evaluation and prediction, 1,3,5-triisopropylcyclohexane was chosen to serve this need. This fluid is not commercially available; therefore, very few thermophysical property measurements exist, and the thermal decomposition kinetics have not yet been investigated. In this work, we study the thermal decomposition kinetics of 1,3,5-triisopropylcyclohexane between 350 and 425 °C. The decomposition reactions were performed in stainless-steel ampule reactors. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by use of gas chromatography. These data were used to derive pseudo-first-order rate constants that ranged from 2.38×10^{-7} s^{-1} at 350 °C to 7.28×10^{-5} s^{-1} at 425 °C. The Arrhenius parameters of the thermal decomposition of 1,3,5-triisopropylcyclohexane were measured to be $A = 5.67 \times 10^{16}$ s^{-1} and activation energy $E_a = 279$ kJ/mol. These parameters can be used to estimate decomposition rates at other temperatures and are critical to the successful application of 1,3,5-triisopropylcyclohexane in experimental and modeling studies of surrogate diesel fuels.

■ INTRODUCTION

Kerosene-based fuels, of great importance for civilian, military, and aerospace applications, are complex mixtures with hundreds or even thousands of constituents.[1−3] The complexity and compositional variability of "real" kerosene fuels can be an obstacle to fundamental research and modeling.[1,2] For this reason, the development of simple mixtures (surrogates) that closely approximate the behavior of real fuels is critical for modeling and experimental testing.[1,4] Such surrogate mixtures might contain only a few components or as many as several dozen. Mixture components are typically chosen to represent classes of chemicals in the fuel being modeled, such as linear alkanes, aromatics, etc. A recent study on diesel fuel surrogate mixture development indicated a need for a multiply substituted, low cetane number, high molecular mass monocycloalkane component.[5] The particular compound suggested to meet these needs on the basis of a thermophysical property evaluation and prediction was 1,3,5-triisopropylcyclohexane.

Prior to inclusion of 1,3,5-triisopropylcyclohexane in surrogate fuel mixtures, a complete fluid behavior model for this pure component must be developed. This requires that its thermophysical properties be measured over a wide range of temperatures and pressures. We recently performed the first chemical and thermophysical property measurements on this fluid.[6] After having the compound synthesized (it is not available commercially), the following properties were measured at ambient pressure: retention indices (150−225 °C), refractive indices (20−30 °C), kinematic viscosity (20−100 °C), and density, speed of sound, and compressibility (5−70 °C).

To extend the applicability of the resulting equation of state, the thermophysical properties will need to be measured over a wider range of temperature and pressure values, including temperatures greater than 300 °C and pressures greater than 10 MP. Under these conditions, decomposition is a serious concern because it can affect the validity and quality of the data that are obtained and the performance, lifetime, and safety of the instruments used to collect the data. For example, decomposition of hydrocarbons can lead to the formation of solid deposits[7−9] that may affect instrument performance and that are often difficult to remove. Additionally, 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.[10−16] 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 1,3,5-triisopropylcyclohexane. Rate constants for decomposition of 1,3,5-triisopropylcyclohexane were determined at temperatures from 350 to 425 °C by use of a method that we have previously used for kerosene-based fuels as well as other potential surrogate mixture components.[10,13−15,17,18] With this method, the fluid was thermally stressed in stainless steel ampule reactors and the extent of decomposition as a function of reaction time was measured by gas chromatography. The rate constants can be used to establish operating ranges and residence times for thermophysical property measurements. The Arrhenius parameters for thermal decomposition were determined from the temperature dependence of the rate constants and can be used to predict decomposition rates at temperatures other than those determined experimentally.

■ EXPERIMENTAL SECTION

Chemicals. Reagent-grade acetone and *n*-octane were used as solvents in this work. They were obtained from commercial sources and used as received. All had stated purities of no less than 99%, which is consistent with our own routine analyses of such solvents by gas chromatography.[19,20] The 1,3,5-triisopropylcyclohexane was obtained from Dr. David Mendenhall of Eastern Sources, Inc. The sample was clear and had a syrup like consistency. The purified product was analyzed by gas chromatography by the custom synthesis laboratory and was found to consist of two geometric isomers. The e,e,e-geometry isomer (all *cis*-) was reported to be the major component (88% of total peak area) and the e,e,a-geometry isomer (*cis*-, *cis*-, *trans*-) was the minor component (12% of total peak area).[6] Our own analysis found the same relative amounts of the two major isomers, within experimental uncertainty.[6]

Apparatus. The apparatus used for the decomposition reactions has been described in detail previously,[13−15,17,18] and thus only a brief description is given here. A stainless steel thermostatted block with several sample slots was used to perform the decomposition reactions. A proportional–integral–derivative (PID) controller used feedback from a platinum resistance thermometer to maintain the temperature of the block within 1 °C of the set point value. At a given time, six ampule reactors (made from 316 stainless steel seamless tubing) could be placed into the tight-fitting holes in the block. Each reaction cell was composed of a 5.6 cm length of stainless steel tubing that was sealed on one side and connected to a high-temperature, high-pressure valve on the other. The cells and valves were capable of withstanding a pressure of at least 100 MPa (15,000 psi) at the temperatures used, although the highest pressures reached were 34.5 MPa. Each cell volume was determined gravimetrically from the mass of hexane required to fill it, and the cell volume (on average 0.11 mL) was used for subsequent calculations.

Decomposition Reactions. With an existing (provisional) equation of state for 1,3,5-triisopropylcyclohexane[21] as implemented in REFPROP,[22] we calculated the mass of fluid needed to achieve a pressure of 34.5 MPa (5000 psi) at the given reaction temperature (350, 375, 400, or 425 °C) and cell volume. These conditions mimic the highest pressure and temperature conditions that occur during some physical property measurements. Constant pressure at the start of the decomposition regardless of temperature helps ensure that differences in observed decomposition rates are not due to any pressure dependence of the reactions.

The calculated mass of 1,3,5-triisopropylcyclohexane was added to the cell with a syringe. Sample masses were approximately 0.07 g but varied depending upon the reaction temperature and the exact cell volume. A valve was then affixed to the cell and tightly closed. A single freeze–pump–thaw cycle was performed using liquid nitrogen in order to remove the air from the vapor space in the cell without removing dissolved air from the fluid. This mimics the conditions under which a fuel is actually used (i.e., the fluid contains dissolved air). It is known that auto-oxidation reactions caused by dissolved oxygen are relatively unimportant for fuel decomposition above 250 to 300 °C.[7]

The loaded reactors were inserted into the thermostatted stainless steel block maintained at the desired reaction temperature (350, 375, 400, or 425 °C). This temperature range was chosen because it allowed for reaction times of a convenient length. At 350 °C, the reaction is relatively slow and so reaction times ranged from 24 to 92 h. At 425 °C, the reaction is much faster, so reaction times ranged from 15 to 60 min. We have previously estimated that the effective thermal equilibration (warm-up) time for these sample cells is approximately 2 min for a reaction temperature of 450 °C.[17] All temperatures used here are lower and so the equilibration time will be even shorter.

The reactors were maintained at the reaction temperature for the specified time period. Although only the cell tubing containing the fluid was inserted into the thermostatted block, the entire reactor was inside the thermostat, minimizing fluid reflux inside the cells. After the reaction time had elapsed, the reactors were removed from the thermostatted block and immediately cooled in room-temperature water to stop the thermal decomposition. The thermally stressed liquid phase was then recovered and analyzed as described below.

Analysis of Liquid-Phase Decomposition Products by GC. The production of volatile decomposition products caused the pressure in the reactors to increase during the thermal decomposition reactions. Even when cooled to room temperature, the reactor cells contained a pressurized mixture of vapor and liquid. When preparing the samples for GC analysis, it was critical to minimize flash and evaporative losses from the samples. Therefore, a sampling procedure was designed to minimize the loss of the liquid sample when the reactors were opened. Specifically, a short length of stainless steel tubing was connected to the valve outlet on the reactor. The end of this tubing was placed inside a chilled (7 °C) glass vial, and the valve was slowly opened. Usually some of the reacted fuel was expelled into the vial, especially for the more thermally stressed samples. The valve was then removed from the reactor, and any liquid remaining in the cell was transferred by syringe to the chilled glass vial. The vial was quickly sealed with a PTFE-coated silicone septum closure, and the mass of the liquid sample was determined. Then, the liquid sample was immediately diluted with a known amount of *n*-octane. This solvent was used because it does not interfere with the GC analysis of any decomposition products. The resulting *n*-octane solution typically had a concentration of 5% reacted 1,3,5-triisopropylcyclohexane (mass/mass).

After heating, the fluid was typically clear and colorless, although some samples heated at the higher temperatures (400 and 425 °C) were slightly yellow. The same slight coloration was observed after the measurement of the normal boiling temperature.[6] Particulate matter was not seen in the fluid after heating, even in the case of the most thermally stressed samples. After each run, the cells and valves were rinsed thoroughly with acetone and also sonicated with solvent for 5 min to remove any solid deposits that may have formed. Cleaned cells and valves were heated to 110 °C for 1 h to remove residual solvent. Blank experiments were occasionally performed to check the effectiveness of this cleaning protocol. For these blank experiments, a cell was loaded with fuel as described above, but the cell was not heated above room temperature. After a week, the fuel in the cell was removed and analyzed by gas chromatography (GC) as described in the following section. The success of the cleaning and drying procedure was confirmed by the visual absence of color or solids in the unheated fuel and by the absence of acetone or 1,3,5-triisopropylcyclohexane decomposition products in the resulting gas chromatogram.

A gas chromatograph equipped with a flame ionization detector (FID) was used to analyze the extent of decomposition of the samples. Aliquots (1 μL) from the crimp-sealed vials were injected by use of an automated sampler. 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 0.25 μm film of (5% phenyl)methylpolysiloxane. A 40:1 split ratio was used. The temperature program consisted of an initial isothermal separation at 80 °C for 4 min, followed by a 20 °C/min gradient to 280 °C.

For selected samples, the thermal decomposition products were analyzed with gas chromatography–mass spectrometry in order to identify the products. The column and temperature program were identical to those described in the previous paragraph for GC-FID analysis. Mass spectra were collected for each peak from 40 to 550 relative molecular mass (RMM) units. Peaks were identified with guidance from the NIST/EPA/NIH mass spectral database and also on the basis of retention indices.[19,23]

■ RESULTS AND DISCUSSION

Using GC−MS, we identified the products of a 2 h decomposition reaction at 400 °C. Table 1 shows the most abundant compounds, based on % of total peak area. The % area cutoff used was 0.15%. The solvent and remaining 1,3,5-triisopropylcyclohexane peaks were subtracted prior to peak integration. The measured decomposition products fall into one of three categories: substituted cycloalkanes (partially

desubstituted 1,3,5-triisopropylcyclohexane), substituted aromatics, or light, branched, olefinic hydrocarbons. We deduce from the emergent suite that the cracking that is occurring during heating is mainly thermal, although the presence of approximately 28% aromatic products suggests that a catalytic cracking mechanism may be playing a role as well.[24]

While a detailed mechanism of the pyrolysis of 1,3,5-triisopropylcyclohexane is not known, we can make a few statements on the basis of the observed decomposition products listed in Table 1. For example, we note the presence of several products that are potentially the result of β-scission, such as 1,3-diisopropylcyclohexane and (1-methylethyl)-benzene. We also observed the formation of several substituted aromatic products that are potentially the result of catalytic dehydrogenation, likely occurring on the 316 stainless steel cell walls (this material can have 16−18% chromium and 10−14% nickel, mass/mass).

For kinetic analysis, decomposition was quantified by measuring the percent of 1,3,5-triisopropylcyclohexane that remained after thermal stress, as determined by peak areas. This use of relative GC peak areas for the kinetic analysis is possible because of the types of compounds being analyzed and the use of a flame ionization detector. For hydrocarbons, the relative sensitivity of the detector (on the basis of moles of carbon) varies by only a few percent.[25] Consequently, calibrating the detector for each individual compound is unnecessary as it would not be expected to significantly change the measured rate constants.

As seen in Figure 1, the chromatogram of unheated 1,3,5-triisopropylcyclohexane (retention time = 9.5 min) contains

Table 1. Summary of 1,3,5-Triisopropylcyclohexane Thermal Decomposition Products Produced after 2 h at 400 °C

| compound	% of total area
2-methyl-1-propene	0.17
2-methylbutane	0.47
2-pentene	1.45
2,3-dimethyl-1-butanol	1.28
2,3-dimethyl-2-butene	0.62
benzene	0.40
2,5-dimethylhexane	0.44
2,6-dimethyl-3-heptene	0.35
2-methyl-2-octene	0.69
ethylbenzene	1.61
p-xylene	0.40
o-xylene	0.40
2,3-dimethyl-1,3-heptadiene	0.33
(1-methylethyl)benzene	5.41
(1-methylethylidene)cyclohexane	1.10
2,6-dimethyl-2-octene	2.27
1-ethyl-3-methylbenzene	0.65
1-methyl-3(1-methylethyl)benzene	0.68
1-methyl-2-(1-methylethyl)benzene	0.79
1-ethyl-3-(1-methylethyl)benzene	5.98
1,3-diisopropylcyclohexane	17.27
1-methyl-3,5-bis(1-methylethyl)benzene	2.84
1,5-diisopropyl-2,3-dimethylcyclohexane	11.11
1,3-diisopropyl-2,3-dimethylcyclohexane	4.59
1,3-diisopropyl-5-ethylidenecyclohexane	11.44
1,3-diisopropyl-5-ethenylcyclohexane	15.62
1,3,5-tris(1-methylethyl)benzene	8.68
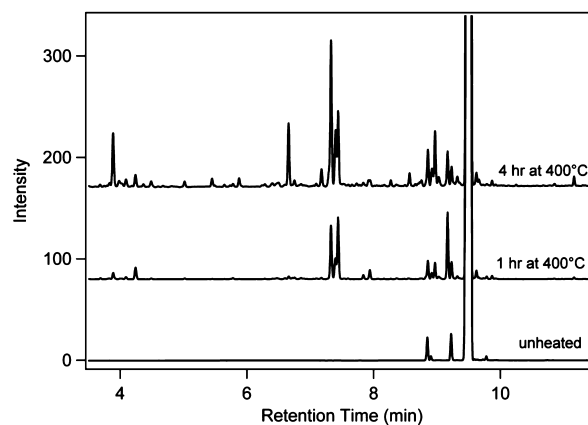
Figure 1. Gas chromatograms of unheated 1,3,5-triisopropylcyclohexane and of two samples of thermally decomposed 1,3,5-triisopropylcyclohexane. The heated samples had been maintained at 400 °C for 1 and 4 h, which respectively caused about 6% and 17% of the 1,3,5-triisopropylcyclohexane to decompose. The large peak at 9.5 min is unheated 1,3,5-triisopropylcyclohexane.

few very impurity peaks, and the total area of these peaks is 0.040%. Note that the two isomers of 1,3,5-triisopropylcyclohexane are not baseline-resolved, and they appear as one large peak in the chromatograms in Figure 1. Figure 1 also contains chromatograms of 1,3,5-triisopropylcyclohexane that was thermally stressed at 425 °C for 1 and for 4 h. After 1 h at 425 °C, several decomposition products have formed, most with retention times longer than 7 min. On the basis of peak areas, it is found that 6% of 1,3,5-triisopropylcyclohexane has decomposed after 1 h at 425 °C. After 4 h at 425 °C, many

more decomposition products have formed including lighter species with shorter retention times. On the basis of peak areas, 17% of 1,3,5-triisopropylcyclohexane has decomposed after 4 h at 425 °C.

The kinetic analysis was done by monitoring the percentage loss of 1,3,5-triisopropylcyclohexane as a function of reaction time, t. At each of the four temperatures, data were collected at four different reaction times, with at least three replicate decomposition reactions run at each reaction time. Pseudo-first-order rate constants, k, for decomposition were obtained by fitting these data to a first-order rate law, eqs 1–3, where A represents 1,3,5-triisopropylcyclohexane and B represents the sum of all thermal decomposition products:

$$A \rightarrow B \tag{1}$$
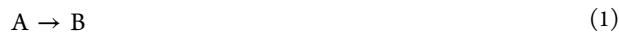
$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} = kt \tag{2}$$

$$\ln[A]_t = \ln[A]_0 - kt \tag{3}$$

Using eq 3, the half-life ($t_{0.5}$), the time required for one-half of the 1,3,5-triisopropylcyclohexane to decompose, and $t_{0.01}$, the time required for 1% of the 1,3,5-triisopropylcyclohexane to decompose, were calculated. Finally, the pseudo-first-order rate constants for thermal decomposition were used to evaluate the parameters of the Arrhenius equation, eq 4, where E_a is the activation energy of decomposition, A is the pre-exponential term, T is the temperature (in K), and R is the gas constant:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

The data for the decomposition reactions at 400 °C are shown in Figure 2. The value of k at 400 °C, obtained from the slope
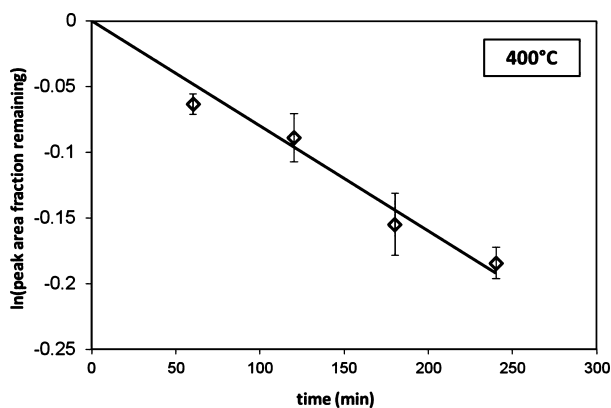

Figure 2. Plot of the ln(1,3,5-triisopropylcyclohexane peak area fraction remaining) as a function of time at 400 °C. Each data point represents the average of at least three individual decomposition reactions, and the uncertainty represents the standard deviation of multiple experiments. The pseudo-first-order rate constant for the decomposition reaction was determined from the slope of the linear fit to the data.

of the linear fit in Figure 2, is 1.34×10^{-5} s^{-1}. The standard uncertainty of 5.33×10^{-7} s^{-1} was obtained from the uncertainty in the linear fit constrained through zero.

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 uncertainties given in Table 1 were calculated from the standard deviation of replicate measurements, the uncertainty

Table 2. Kinetic Data Based on the Assumption of First Order for the Thermal Decomposition of 1,3,5-Triisopropylcyclohexane

T (°C)	k (s^{-1})	uncertainty in k (s^{-1})	$t_{0.5}$ (h)	$t_{0.01}$ (min)
350	2.31×10^{-7}	9×10^{-9}	835	726
375	1.78×10^{-6}	1.4×10^{-7}	108	94.3
400	1.34×10^{-5}	5×10^{-7}	14.4	12.5
425	7.28×10^{-5}	2.9×10^{-6}	2.65	2.30

in the area standardization, and the standard error in the linear fit. The values of $t_{0.5}$ and $t_{0.01}$ show that apparatus residence times of several hours may be acceptable for property measurements at 350 °C but not at 425 °C.

An Arrhenius plot of the pseudo-first-order rate constants for thermal decomposition of 1,3,5-triisopropylcyclohexane is shown in Figure 3. The Arrhenius parameters determined
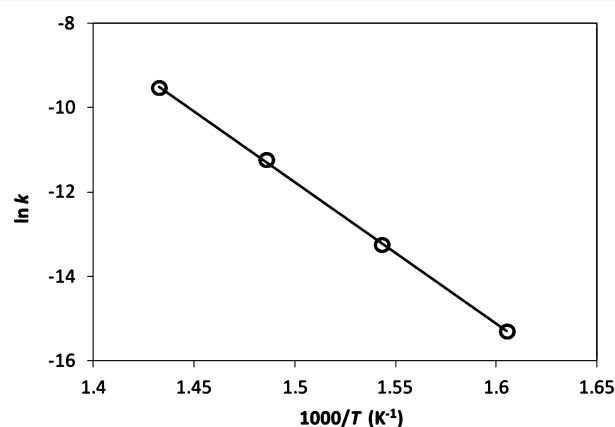

Figure 3. Arrhenius plot for the decomposition of 1,3,5-triisopropylcyclohexane. No error bars are shown because the uncertainties in the values of ln k are smaller than the symbols. The Arrhenius parameters determined from the fit to the data are $A = 5.67 \times 10^{16}$ s^{-1} and $E_a = 279$ kJ·mol^{-1}.

from a linear regression of the data were $A = 5.67 \times 10^{16}$ s^{-1} and $E_a = 279$ kJ·mol^{-1}. The standard uncertainty in E_a, calculated from the standard error in the slope of the regression, was 4 kJ·mol^{-1}. The Arrhenius plot shown in Figure 3 is quite linear ($r^2 > 0.999$) over the 75 °C temperature range of these experiments. This suggests that our use of first-order kinetics is justified despite the oversimplification of the reaction in eq 1.

The measured activation energy of 279 kJ·mol^{-1} is much smaller than the bond energy of a carbon−carbon bond. The initial decomposition mechanism of 1,3,5-triisopropylcyclohexane likely involves scission of the C−C bond between the cyclohexane ring and an isopropyl group. The bond energy of this C−C bond, although not known, is likely similar to that of the central C−C bond in 2,3-dimethylbutane, which is 353 kJ/mol.[26] The much smaller activation energy we have measured for thermal decomposition suggests that other processes and reactions are occurring, likely chain processes. Therefore, we want to emphasize that we are reporting an overall or global rate constant for the thermal decomposition of 1,3,5-triisopropylcyclohexane and its intermediate reaction products, and not a rate constant for the initial reaction.

The thermal stability of saturated hydrocarbons has been the subject of much research, and certain stability trends have been observed. For example, saturated hydrocarbons with tertiary

carbons (from branching or ring substitution) are less thermally stable than related compounds that do not have tertiary carbons.[27,28] To illustrate, at 427 °C the pseudo-first-order rate constant for decomposition is 2.62×10^{-6} s^{-1} for cyclohexane (zero tertiary carbons), 3.83×10^{-6} s^{-1} for methylcyclohexane (one tertiary carbon), 2.34×10^{-5} s^{-1} for n-propylcyclohexane (one tertiary carbon), and 3.58×10^{-5} s^{-1} for isopropylcyclohexane (two tertiary carbons).[28] To the best of our knowledge, no other measurements of the thermal stability of 1,3,5-triisopropylcyclohexane have been reported; therefore, a direct comparison to previous values is not possible. However, a similar kinetic analysis has been reported for n-propylcyclohexane over a similar temperature range.[17] As expected, the highly branched 1,3,5-triisopropylcyclohexane (six tertiary carbons) is less stable than n-propylcyclohexane. In fact, the first-order rate constant for the thermal decomposition of 1,3,5-triisopropylcyclohexane is approximately 5 times larger than the rate constant for n-propylcyclohexane for temperatures between 375 and 425 °C. As an example, the rate constant for the thermal decomposition of n-propylcyclohexane at 425 °C was reported to be 1.59×10^{-5} s^{-1}, compared to 7.28×10^{-5} s^{-1} for 1,3,5-triisopropylcyclohexane (Table 1). This is a large enough difference to have significant implications for engine tests or high-temperature property measurements.

CONCLUSIONS

We measured the kinetic parameters for the thermal decomposition of 1,3,5-triisopropylcyclohexane, a potential component of a surrogate for kerosene-based fuels. This fluid is important because it provides a unique and critical ingredient for a diesel fuel surrogate: a multiply substituted, low cetane number, high molecular mass monocycloalkane. Pseudo-first-order rate constants were measured from 350–425 °C and at an initial pressure of 34.5 MPa. We derived Arrhenius parameters of $A = 5.67 \times 10^{16}$ s^{-1} and $E_a = 279$ kJ·mol^{-1} for the decomposition of 1,3,5-triisopropylcyclohexane. The first-order rate constants of decomposition of 1,3,5- triisopropylcyclohexane are 5 times larger than those of n-propylcyclohexane at a given temperature, demonstrating the thermal instability of tertiary carbons. These kinetic values will be useful for planning physical and chemical property measurements at high temperatures and pressures. However, it is important to remember that the kinetics of decomposition may depend on pressure and also on the identity of the wetted surfaces of the apparatus. Strictly speaking, these results are best applied for pressures near 35 MPa and when the wetted surface is constructed from 300 series stainless steels.

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Notes
The authors declare no competing financial interest.

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