Combustion and Flame 157 (2010) 2078–2085

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

A detailed experimental study of *n*-propylcyclohexane autoignition in lean conditions

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ARTICLE INFO

Article history:
Received 16 December 2009
Received in revised form 9 April 2010
Accepted 16 April 2010
Available online 14 May 2010

Keywords:
n-Propylcyclohexane
Autoignition
Rapid compression machine
Diesel surrogate

ABSTRACT

The autoignition chemistry of lean *n*-propylcyclohexane/"air" mixtures ($\phi = 0.3, 0.4, 0.5$) was investigated in a rapid compression machine at compressed gas temperatures ranging from 620 to 930 K and pressures ranging from 0.45 to 1.34 MPa. Cool flame and ignition delay times were measured. Cool flame delay times were found to follow an Arrhenius behavior, and a correlation including pressure and equivalence ratio dependences was deduced. The present ignition delay data were compared with recent experimental results and simulations from the available thermokinetic models in the literature. Negative temperature coefficient zones were observed when plotting ignition delay times versus compressed gas temperature. The oxidation products were identified and quantified during the ignition delay period. Formation pathways for the C_9 bicyclic ethers and conjugate alkenes are proposed. The experimental data provide an extensive database to test detailed thermokinetic oxidation models.

1. Introduction

In spite of their large content in Diesel or jet fuels [1], large cycloalkanes have been the subject of few research studies. Their presence in large proportions in oil sands also pushes towards exploring their combustion properties. The use of these particular fuels in new engine concepts such as Homogeneous Charge Compression Ignition (HCCI) or Narrow Angle Direct Injection (NADI) [2] requires a deep understanding of the chemistry responsible for their autoignition, both at low and high temperatures. In this context, experimental studies over large ranges of pressure, temperature, and equivalence ratio are required to test and validate detailed thermokinetic oxidation models for these fuels.

This work explores the autoignition and oxidation at high pressure of a molecule of particular interest for surrogate Diesel fuels [3]: *n*-propylcyclohexane (PCH). It follows a series of work aiming for a better understanding of autoignition and oxidation of alkylcyclohexanes. Cyclohexane and methylcyclohexane autoignitions have been studied at high pressures and temperatures in shock tubes [4,5]. Ignition delay times were measured at equivalence ratios 0.25, 0.5, and 1 between 847 and 1379 K at pressures ranging from 11 to 61 atm for cyclohexane, and between 881 and 1319 K at pressures ranging from 10.8 to 69.5 atm for methylcyclohexane. Methylcyclohexane autoignition has also been investigated in a shock tube at pressures from 1 to 50 atm, temperatures from 795 to 1560 K, and equivalence ratios from 0.5 to 2.0 [6]. Sivaramakrishnan and Michael [7] have measured high-temperature rate constants for the attack by ·OH on cyclohexane and methylcyclohexane in a shock-tube. Alkylcyclohexanes have also been the subject of several low temperatures studies, most notably in rapid compression machines. Lemaire et al. [8] have reported ignition delay time measurements as well as intermediate species concentration profiles between 600 and 900 K, and 7–14 atm. These data have been used to validate a detailed thermokinetic model [9]. Pitz et al. [10] have conducted an experimental and modeling study on methylcyclohexane autoignition. More recently, Mittal and Sung [11] have studied methylcyclohexane autoignition in a rapid compression machine at equivalence ratios from 0.5 to 1.5, compressed charge pressures of 15.1 and 25.5 bar, and temperatures between 680 and 905 K. Cyclohexane and methylcyclohexane have also been studied in motored engine conditions [12], showing an increase of reactivity with the presence of a methyl group on the cyclane.

The autoignition and oxidation of heavier alkylcyclohexanes have also been studied at high temperatures. Oehlschlaeger's group extended their work on cycloalkanes by measuring ignition delay times of ethylcyclohexane in a shock tube [5] at pressures from 10.8 to 69.5 atm, temperatures from 881 to 1319 K, and equivalence ratios of 0.25, 0.5, and 1.0. Finally, PCH oxidation has been studied in a jet-stirred reactor between 900 and 1200 K at the atmospheric pressure and equivalence ratios ranging from 0.5 to 1.5 [13]. The resulting model was extended to low-temperatures as part of a study on Diesel surrogate fuels [14]. PCH combustion in doped premixed laminar flames has also been investigated

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doi:10.1016/j.combustflame.2010.04.012

experimentally and simulated with a model containing 322 species in 2146 reactions [15].

The objective of this study is to investigate the low-temperature oxidation and autoignition of PCH in order to provide an extensive set of new experimental data at high pressures (0.45–1.34 MPa), low temperatures (620–930 K), and in lean conditions (ϕ = 0.3, 0.4, 0.5).

2. Experimental

Autoignition experiments were performed for lean (ϕ = 0.3, 0.4, 0.5) PCH/"air" mixtures in a rapid compression machine (RCM), which has been described elsewhere [16]. The compression ratio was 9.5. The initial pressure varied from 33.3 to 66.7 kPa, leading to pressures at the end of compression (EOC) from 0.45 to 1.34 MPa. The compression time was fixed at 60 ms, in order to limit vortex formation [17] during the compression and consequently temperature inhomogeneities in the chamber after the EOC. The temperature was varied by changing the composition of the inert gas in "air": nitrogen was replaced by argon to reach higher compressed gas temperatures and by carbon dioxide to reach lower ones. The temperature T_c at the EOC was calculated from the pressure at the EOC p_1, the initial pressure p_0 and the initial temperature T_0, according to the adiabatic core gas model [18]. The investigated range of temperatures was 620–930 K. The reactant used was HPLC grade from Sigma Aldrich Chemicals. Dissolved gases were removed by successive freezing/pumping cycles. The compositions of the mixtures studied are given in Table 1. The mixtures were prepared 24 h in advance before use with a total pressure of 133.3 kPa. As the PCH vapour pressure is below 400 Pa at room temperature [19], the glass vessels in which the mixtures were prepared were heated at 353 K, and the RCM cylinder and combustion chamber at 363 K, ensuring that the PCH vapour pressure exceeded 8 kPa at all locations. The temperature was measured using a thermocouple along the way, to make certain of the absence of cold spots in the tubing, the glass vessels, and the combustion chamber.

Table 1
Composition of the PCH/O_2/inert mixtures used for the autoignition studies and corresponding temperature T_c.

Mole fraction					T_c/K
PCH	O_2	N_2	Ar	CO_2	
(a) ϕ = 0.5					
0.0077	0.2084	0.3606	0.0000	0.4233	622
0.0077	0.2084	0.4880	0.0000	0.2959	643
0.0077	0.2084	0.6036	0.0000	0.1803	663
0.0077	0.2084	0.7055	0.0000	0.0784	685
0.0077	0.2084	0.7839	0.0000	0.0000	701
0.0077	0.2084	0.6271	0.1568	0.0000	716
0.0077	0.2084	0.7055	0.0784	0.0000	716
0.0077	0.2084	0.5362	0.2477	0.0000	751
0.0077	0.2084	0.3919	0.3919	0.0000	787
0.0077	0.2084	0.1960	0.5869	0.0000	823
0.0077	0.2084	0.2799	0.5040	0.0000	824
0.0077	0.2084	0.1176	0.6663	0.0000	853
0.0077	0.2084	0.0549	0.7290	0.0000	867
0.0077	0.2084	0.0000	0.7839	0.0000	882
(b) ϕ = 0.4					
0.0062	0.2087	0.3611	0.0000	0.4240	634
0.0062	0.2087	0.4946	0.0000	0.2905	653
0.0062	0.2087	0.6045	0.0000	0.1806	673
0.0062	0.2087	0.7066	0.0000	0.0785	695
0.0062	0.2087	0.7851	0.0000	0.0000	715
0.0062	0.2087	0.6281	0.1570	0.0000	752
0.0062	0.2087	0.5370	0.2481	0.0000	768
0.0062	0.2087	0.3925	0.3926	0.0000	795
0.0062	0.2087	0.2803	0.5048	0.0000	821
0.0062	0.2087	0.1963	0.5888	0.0000	848
0.0062	0.2087	0.1178	0.6673	0.0000	865
0.0062	0.2087	0.0551	0.7300	0.0000	878
0.0062	0.2087	0.0000	0.7851	0.0000	900
(c) ϕ = 0.3					
0.0047	0.2090	0.3617	0.0000	0.4246	640
0.0047	0.2090	0.3932	0.0000	0.3932	644
0.0047	0.2090	0.4952	0.0000	0.2911	661
0.0047	0.2090	0.5272	0.0000	0.2591	668
0.0047	0.2090	0.6054	0.0000	0.1809	683
0.0047	0.2090	0.6290	0.0000	0.1573	687
0.0047	0.2090	0.7077	0.0000	0.0786	704
0.0047	0.2090	0.7863	0.0000	0.0000	724
0.0047	0.2090	0.6290	0.1573	0.0000	761
0.0047	0.2090	0.5378	0.2485	0.0000	783
0.0047	0.2090	0.3931	0.3932	0.0000	817
0.0047	0.2090	0.2807	0.5056	0.0000	838
0.0047	0.2090	0.1966	0.5897	0.0000	871
0.0047	0.2090	0.1179	0.6684	0.0000	892
0.0047	0.2090	0.0550	0.7313	0.0000	917
0.0047	0.2090	0.0000	0.7863	0.0000	940

Pressure and light emission profiles were recorded with a 40 μs time step during each experiment and used to measure cool flame and ignition delay times. The pressure signal was acquired with a Kistler 601A pressure transducer, and the light emission signal with a RCA 1P21 photomultiplier equipped with a blue filter centered on a wavelength of 400 nm. Fig. 1 shows an example of pressure and light emission profiles in the case of a two-stage ignition. The cool flame delay time was measured as the elapsed time between the EOC and the maximum of light emission associated to the cool flame occurrence. The ignition delay time was defined as the elapsed time between the EOC and the start of ignition. As in the case of the lowest temperatures and/or lean mixtures, the pressure jump associated with the ignition was not sharp enough to precisely identify the start of ignition, it was defined as the crossing point between the line tangent to the pressure signal before the pressure jump and the line tangent to the pressure signal at the point of maximum slope dp/dt, as shown in the close-up of Fig. 1. Tables containing the ignition and cool flame delay times are available as Supplementary material. Non-reactive mixtures were also prepared by replacing oxygen by nitrogen, which has a heat capacity similar to that of oxygen. They were compressed following the same procedure as the reactive mixtures. The corresponding pressure signals could be used to include heat losses in modeling by considering an adiabatic volume expansion, as described in [20]. The pressure profiles of non-reactive mixtures are available upon request to the authors.

At chosen moments during the ignition delay, samples were withdrawn from the RCM chamber by rapid quenching of the reacting mixture into a sampling vessel, as described previously [21]. PCH and stable intermediate oxidation products formed

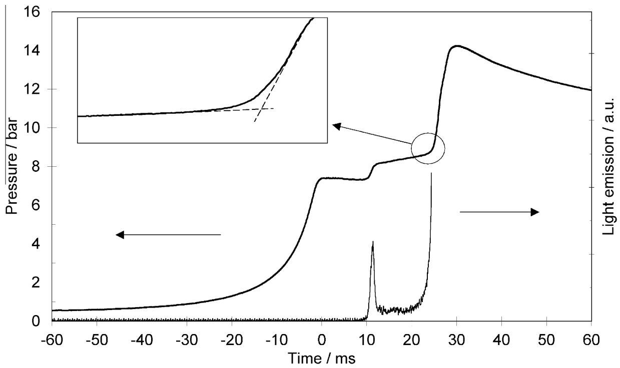

Fig. 1. Example of pressure and light emission-time profiles during a two-stage ignition of PCH. p_1 = 0.68 MPa, T_c = 660 K, ϕ = 0.5. On the top-left, a close-up showing the methodology of determination of the start of ignition.