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Influence of the double bond position on the oxidation of decene isomers at high pressures and temperatures

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Abstract

High pressure, single pulse shock tube oxidation experiments were conducted in order to probe the chemical kinetic effects of the double bond position in long alkenes. All oxidation experiments were carried out with approximately 100 ppm of 1-decene, cis-2-decene, cis-5-decene, and trans-5-decene, in argon, at stoichiometric conditions. The experimental conditions covered the pressure range of 40–66 bar and temperature range of 850–1500 K, with an average reaction time of 2 ms. Gas chromatographic measurements of the stable intermediates indicated increased reactivity for the isomers with more centrally located double bonds, with no influence from the cis–trans configuration observed at these conditions. Significantly different yields in most of the intermediate species measured were observed. Chemical kinetic models were assembled with the aid of Reaction Mechanism Generator where these are able to adequately predict the major product species of all isomers investigated. Simulation of the experiments indicates significantly different reaction pathways that each decene isomers undergoes, controlled entirely by the position of the double bond. The implication for fuels with such molecular structure is that reactivity, as well as pollutant formation characteristics can be significantly different depending on the position of the double bond in very similar molecules.
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1. Introduction

Biodiesel, a promising renewable fuel, primarily consists of mixtures of long-chain fatty acid methyl esters (FAMEs), which are derived from waste animal fats and vegetable oils. The degree of saturation in a biodiesel is one molecular characteristic that can vary widely depending on the feedstock [1]. It has been shown to influence the particulate matter (PM) emissions [2] as well as the NO_x emissions [1,3–5]. It has also been observed that the position of the double bonds, as well as the cis–trans isomerism, influences the

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ignition delay and engine performance of not only unsaturated biodiesel molecules, but long alkenes as well [6–11], where these are present in biodiesel/petroleum diesel blends.

A limited number of studies have focused on understanding the chemical kinetic effects of the double bond position. Experimental studies in the literature have focused on low temperature ignition measurements of C5–C7 alkenes and C9 FAMEs [6–8]. A decrease in the reactivity has been observed at temperatures below 900 K, when the double bond is more centrally located. The only exception in experimental studies being the work of Hellier et al., [10] who found a non-linear relationship among octene isomers in a modern diesel engine and a strong influence from the cis–trans isomerism, where the theory behind the latter phenomenon is discussed by Bounaceur et al. [12].

Few modeling studies have investigated the chemical kinetic effects of the double bond position [11–14]. Furthermore, limited intermediate and high temperature experimental data are available, despite models suggesting an inversion in the reactivity for alkene isomers at high temperatures [11,13]. To date, only Mehl et al. [11] have gathered high temperature ignition delay data for C5–C6 linear alkene isomers, demonstrating this inversion of reactivity. In their work, a chemical kinetic model was developed which was able to capture the low to high temperature ignition trends of the investigated alkenes.

The only relevant high temperature experiments on FAMEs were conducted by Wang et al. [15]. Ignition delay times for methyl 9-decenoate and methyl trans-5(6)-decenoates were compared and found to be indistinguishable at temperatures above 900 K, while significantly different below 900 K. These high temperature results are in contrast with those of Mehl et al. [11], and may indicate a difference in the reactivity trends between unsaturated FAMEs and their side-chain analogs. The results of Wang et al. [15] were simulated using kinetic models developed by Herbinet et al. [14] but these only qualitatively agreed with their data.

To further elucidate the influence of the double bond position on the reactivity of alkenes and biodiesel molecules in the high temperature regime, experiments have been conducted in this study with four commercially available decene isomers, including 1-decene ($C_{10}H_{20}$-1), cis-2-decene (c-$C_{10}H_{20}$-2), cis-5-decene (c-$C_{10}H_{20}$-5), and trans-5-decene (t-$C_{10}H_{20}$-5) at the University of Illinois at Chicago in the high pressure, single pulse shock tube (HPST). The long decene isomers are representative of the alkenyl side chain of real biodiesel fuels (C11 FAMEs), and the cis configuration is naturally found in fatty acids used in biodiesel production, with trans configurations introduced artificially in small amounts [1]. This study presents the experimental results for the decene isomers, to our knowledge the first for these molecules, while three models developed with the aid of Reaction Mechanism Generator (RMG) [16] were used to interpret the results. This work is part of an effort to build a comprehensive experimental and kinetic validation database in order to develop accurate chemical kinetic models for the oxidation of real biodiesel fuels.

2. Experimental method

The details of the construction and the operation of the HPST have been presented previously [17], and will not be discussed here. The average reaction temperatures behind reflected shocks were determined using the external chemical thermometer technique [18,19]. Temperatures up to 1300 K have an estimated systematic uncertainty of ±15 K, increasing to ±30 K at 1500 K. Random error is represented as scatter in the data reported here.

Test mixtures with oxygen (99.999% purity Airgas) and approximately 100 ppm of each fuel (equivalence ratio $\varphi \approx 1$) in argon (99.999% purity Airgas) were prepared in a heated 40 L, high pressure vessel. The mixtures were prepared manometrically for all olefins (after degassing using a freeze–thaw process). The purity of 1-decene, cis-5-decene, trans-5-decene, cis-2-decene were $\geqslant$97% (Sigma–Aldrich), 96% (GFS Chemicals), 97% (GFS Chemicals), >95% (TCI Chemicals), respectively. All species calibrations were done using standard gaseous calibration mixtures from Sigma–Aldrich and Restek, with the exception of the parent fuels, for which the calibration mixtures were prepared manometrically. The relative uncertainties in the calibrations are estimated to be ±10% for all species.

The post-shock gases were withdrawn using the online GC sampling technique [20] and analyzed using flame ionization and thermal conductivity detectors. The product species were identified by a combination of an HP 5973 mass selective detector (MSD) and measurement of retention times for authentic standards. The experiments for each molecule were conducted by sweeping a temperature range of 850–1500 K while also covering a narrow range of pressures (40–66 ± 1 bar) and reaction times (1.3–2.4 ± 0.1 ms). The experimental results are presented as mole fractions (ppm) of all the measured stable intermediates as a function of the reaction temperature.

3. Experimental results

A total of 126 experiments were conducted for all the molecules investigated. The major stable intermediates detected in all cases were CO,

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