

A shock tube study of C4–C6 straight chain alkenes + OH reactions

Fethi Khaled^a, Jihad Badra^b, Aamir Farooq^{a,*}

^a Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

^b Fuel Technology Division, R&D Center, Saudi Aramco, Dhahran 31311, Saudi Arabia

Received 3 December 2015; accepted 3 June 2016

Available online 21 June 2016

Abstract

Alkenes are known to be good octane boosters and they are major components of commercial fuels. Detailed theoretical calculations and direct kinetic measurements of elementary reactions of alkenes with combustion radicals are scarce for C4 alkenes and they are practically absent for C5 and larger alkenes. The overall rate coefficients for the reaction of OH radical with 1-butene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$, k_{I}), 1-pentene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$, k_{II}), cis/trans 2-pentene ($\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$, k_{III} and k_{IV}), 1-hexene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, k_{V}) and cis/trans 2-hexene ($\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$, k_{VI} and k_{VII}) were measured behind reflected shock waves over the temperature range of 833–1377 K and pressures near 1.5 atm. The reaction progress was followed by measuring mole fraction of OH radicals near 306.7 nm using UV laser absorption technique. It is found that the rate coefficients of OH + trans-2-alkenes are larger than those of OH + cis-2-alkenes, followed by OH + 1-alkenes. The derived Arrhenius expressions for the overall rate coefficients (in $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) are:

$$k_{\text{I}} = (4.83 \pm 0.03)10^4 \cdot T^{2.72 \pm 0.01} \cdot \exp\left(\frac{940.8 \pm 2.9 \text{ cal/mol}}{RT}\right) \quad (946 \text{ K} - 1256 \text{ K})$$

$$k_{\text{II}} = (5.66 \pm 0.54)10^{-1} \cdot T^{4.14 \pm 0.80} \cdot \exp\left(\frac{4334 \pm 227 \text{ cal/mol}}{RT}\right) \quad (875 \text{ K} - 1379 \text{ K})$$

$$k_{\text{III}} = (3.25 \pm 0.12)10^4 \cdot T^{2.76 \pm 0.5} \cdot \exp\left(\frac{1962 \pm 83 \text{ cal/mol}}{RT}\right) \quad (877 \text{ K} - 1336 \text{ K})$$

$$k_{\text{IV}} = (3.42 \pm 0.09)10^4 \cdot T^{2.76 \pm 0.5} \cdot \exp\left(\frac{1995 \pm 59 \text{ cal/mol}}{RT}\right) \quad (833 \text{ K} - 1265 \text{ K})$$

$$k_{\text{V}} = (7.65 \pm 0.58)10^{-4} \cdot T^{5 \pm 1} \cdot \exp\left(\frac{5840 \pm 175 \text{ cal/mol}}{RT}\right) \quad (836 \text{ K} - 1387 \text{ K})$$

$$k_{\text{VI}} = (2.58 \pm 0.06)10^6 \cdot T^{2.17 \pm 0.37} \cdot \exp\left(\frac{1461 \pm 55 \text{ cal/mol}}{RT}\right) \quad (891 \text{ K} - 1357 \text{ K})$$

$$k_{\text{VII}} = (3.08 \pm 0.05)10^6 \cdot T^{2.18 \pm 0.37} \cdot \exp\left(\frac{1317 \pm 38 \text{ cal/mol}}{RT}\right) \quad (881 \text{ K} - 1377 \text{ K})$$

© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Alkenes; Hydroxyl radicals; Rate coefficients; Shock tube

1. Introduction

Alkenes are important constituents of practical fuels [1] and are found in varying quantities in gasoline and diesel fuels. The presence of

* Corresponding author. Tel.: +966544700621.

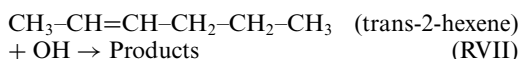
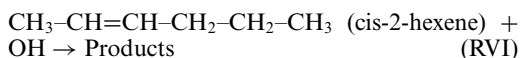
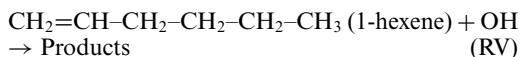
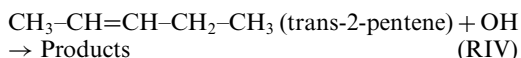
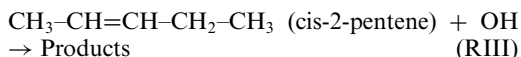
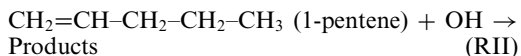
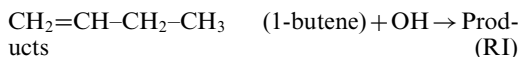
E-mail addresses: aamir.farooq@kaust.edu.sa,
aamir.farooq@gmail.com (A. Farooq).

carbon–carbon double bond gives these molecules special characteristics. Short chain alkenes have a much higher knock resistance than their saturated homologues [2]. Alkenes are also known to impart higher octane sensitivity (RON – MON) to gasoline-like fuels [2,3] and thus these can be used to substitute aromatics. At high concentrations, however, alkenes can alter the stability of the fuel and promote the formations of gums, detrimental for engine injectors [4]. Alkenes are also important combustion intermediates and their production during fuel oxidation represents the first step towards soot formation [5,6].

Due to the importance of alkenes in combustion systems, extensive work has been conducted to study their chemistry [4,7–16]. Mehl et al. [4] examined the auto-ignition behavior of unsaturated hydrocarbons in the low- and high- temperature regimes and proposed a mechanism for the radical pool formation under different temperature regions. Battin-Leclerc [7] performed a detailed study of the formation and decomposition of unsaturated hydrocarbons at high temperatures. Cvetanović [15] studied the reaction of atomic oxygen with different sub-families of unsaturated hydrocarbons, such as normal and cyclic alkenes. The reaction of OH radicals with alkenes has been the focus of several studies due to the critical role of this reaction at combustion relevant conditions [17]. Sumathi et al. [11] developed a detailed estimation scheme to predict H-abstraction reaction rate coefficients by OH radicals from several hydrocarbon and oxygenated families that included alkenes, alkynes, alcohols, aldehydes and acids. The reaction of OH with propene has been studied by several groups in the last two decades [18–21]. A recent experimental study by Badra et al. [21] reported branching ratios of the three H-abstraction channels of propene + OH reaction, while Zador et al. [19] carried out detailed theoretical study of this reaction. Vasu et al. [22] examined the reaction of OH with three butene isomers (1-butene, cis-2-butene and trans-2-butene) in a shock tube facility. They found that the total rate coefficients of the reaction of 1-, cis-2- and trans-2-butene with OH are quite similar, with trans-2-butene being slightly higher. They also reported theoretical branching ratios for the OH + 1-butene reaction over the temperature range of 300–1500 K [22]. Hongyan et al. [14] also conducted a theoretical study of this reaction using transition state theory.

Direct experimental or theoretical studies of longer chain alkenes (C₅ and higher) are scarce in literature. In this work, we present a detailed experimental study of the reaction of OH with C₄, C₅ and C₆ straight chain alkenes. Experiments are carried out under pseudo-first-order conditions using a shock tube and UV laser absorption of OH. The following reactions are investigated over the temperature range of 833–1377 K and pressures

near 1.5:



2. Experimental methods

Experiments were performed behind reflected shock waves in a high vacuum, high purity, stainless steel shock tube facility. Detailed description of the shock tube and the OH laser diagnostic system can be found elsewhere [23]; necessary details are given here. The shock driver and driven sections are 9 m long each with 14.2 cm inner diameter. The test times of all the experiments performed in this work ranged from 1.5 to 2 ms which is more than sufficient for studying the target reactions. The incident shock speed was measured using a series of five piezoelectric PCB pressure transducers that are placed over the last 1.3 m of the driven section of the shock tube. Temperatures and pressures behind reflected shock waves were calculated from the measured incident shock speed and standard shock-jump relations [24]. Uncertainties in the measured shock velocity (≈ 0.05 – 0.1%) translate into uncertainties in the calculated reflected shock temperatures and pressures of about 0.7% and 1%, respectively. The shock tube is connected to a magnetically stirred 24 l mixing vessel and a high purity, high vacuum, sensitive pressure transducer equipped mixing manifold for the preparation of gaseous mixtures.

The OH laser diagnostic and a Kistler 603B piezoelectric pressure transducer are located at a test section 2 cm away from the driven section end-wall. Ultraviolet laser beam for OH detection is generated by the external frequency doubling of red light (614 nm) produced by a ring-dye continuous wavelength (cw) laser which is pumped by a 10 W green laser (532 nm). In the current experiments, the UV light is tuned to the center (306.6868 nm) of the well-characterized R1(5) absorption line in

Download English Version:

<https://daneshyari.com/en/article/6477883>

Download Persian Version:

<https://daneshyari.com/article/6477883>

[Daneshyari.com](https://daneshyari.com)