Revisiting 1-hexene low-temperature oxidation

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ABSTRACT

The low-temperature oxidation of 1-hexene has been studied in a jet-stirred reactor for temperatures from 500 to 1100 K, at atmospheric pressure, for equivalence ratios from 0.5 to 2 with a high dilution in helium. Product formation has been investigated using gas chromatography, as well as laser-single-photon-ionization time-of-flight mass spectrometry and *cw*-cavity-ring down spectroscopy. These two last techniques have allowed the quantification of ketene, C_1–C_3 alkylhydroperoxides, hexenyl hydroperoxides, C_6 unsaturated ketohydroperoxides, and hydrogen peroxide.

Starting from a previous model generated automatically, a new model has been developed for 1-hexene oxidation by updating some determinant reaction kinetics based on newly published theoretical calculations. This new model allows a good prediction of most of the newly obtained experimental results, as well as satisfactory simulation of literature data obtained for the high-temperature oxidation in a high-pressure jet-stirred reactor, in a rapid compression machine, and in two shock tubes.

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1. Introduction

Since alkenes are important components of gasoline [1], the low-temperature oxidation kinetics (below 900 K) of C_5–C_7 linear alkenes was often investigated [2-12]. However, the experimental studies concerning the low-temperature reactivity of the most studied C_5–C_7 alkenes, hexene isomers, which were obtained in a rapid compression machine [4] and in a jet-stirred reactor [10], were limited to stoichiometric conditions. The kinetics of several reactions important for alkene low-temperature oxidation (e.g. reactions of alkenes with OH radicals [13] or reactions of peroxyradicals including a hydroxyl function [14]) was recently investigated using theoretical calculations. However, the last detailed kinetic models of hexene oxidation were published before 2011 by Mehl et al. [7,9] and by Bounaceur et al. [8], except in the case of 3-hexene [11]. In the last case, a model was recently proposed based on that of Mehl et al. [7,9], but with important kinetic parameter fitting and without taking the new theoretically calculated rate constants into account.

The first objective of the present work is then to continue the experimental study of Battin-Leclerc et al. [10] on 1-hexene oxidation made under stoichiometric conditions using a jet-stirred reactor (JSR) with gas chromatography analyses by studying two additional equivalence ratios (0.5 and 2). The second goal is to

expand the range of products analyzed during 1-hexene JSR oxidation by using two additional analytical techniques, *cw*-cavity-ring down spectroscopy (*cw*-CRDS) and laser-ionization mass spectrometry. These techniques have been recently shown successful in quantifying hydrogen peroxide, ketene and hydroperoxides during alkane oxidation [15]. Finally, the third purpose of this paper is to describe a new model for 1-hexene low-temperature oxidation based on recently published theoretical kinetic data.

2. Experimental setup and procedure

A heated isothermal jet-stirred reactor, already used in many organic compounds oxidation studies [16], has been connected to the three following analytical devices:

(1) Gas chromatographs (GCs) via a heated transfer line.
(2) A laser-single-photon-ionization time-of-flight mass spectrometer (SPI-TOF-MS) via capillary-tube sampling.
(3) A *cw*-cavity-ring down spectroscopy (*cw*-CRDS) optical cell using the near-IR wavelength range via sonic probing.

More details about experimental procedure can be found in the Supplementary material (SM).

2.1. Jet-stirred reactor and gas feeding

The reactive mixture entered the spherical JSR made out of quartz through four nozzles, positioned in the center of the reactor. These nozzles were designed in order to ensure a perfect

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gas mixing and to avoid concentration gradients inside the reactor [17]. The reactor was warmed using Thermocoax resistance wires. The reaction temperature was measured by a type K thermocouple positioned at the center of the reactor. The pressure in the reactor (P) was controlled using a needle valve positioned at the downstream of the reactor and taken equal to 106.7 kPa.

A stable, continuous stream of helium, oxygen and 1-hexene to the reactor was ensured thanks to Bronkhorst mass flow controllers. Helium and oxygen were provided by Messer (purities of 99.99% and 99.999%, respectively). 1-Hexene was provided by ALFA AESAR (purity of 98%) and used without further purification. The fuel flow rate to the reactor was controlled using a liquid Coriolis mass flow controller provided by Bronkhorst. The liquid flow was mixed with helium and passed through an evaporator. The fuel/helium blend was subsequently mixed with oxygen. The relative uncertainty in gas flow rates was approximately 5%. To limit thermal gradients inside the reactor, prior to entering the spherical vessel, the gaseous mixture was heated to the reactor temperature in a quartz annular pre-heating zone also using Thermocoax resistance wires. The residence time in this zone was negligible compared to the residence time in the reactor (τ) which was taken equal to 2 s.

2.2. Gas chromatography analyses

The gases leaving the reactors were analyzed using three dedicated GCs. The first GC was equipped with a thermal conductivity detector and a Carbosphere packed column. It was used to quantify O_2, CO and CO_2. The second GC was equipped with a flame-ionization detector and a PlotQ capillary column. The flame-ionization detector was preceded by a methanizer to detect CO, CO_2 and formaldehyde with improved sensitivity. This GC was used to quantify molecules containing up to five carbon atoms. The third GC was equipped with a flame-ionization detector and a HP5-MS capillary column for quantifying molecules containing at least five carbon atoms. Response factors were determined by injecting calibration mixtures or using the effective carbon number method [18]. The exit of the reactor was connected with the aforementioned gas chromatographs through heated transfer lines kept at 423 K to limit condensation problems. The identification of the products has remained the same as in the previous work performed under stoichiometric conditions [10].

2.3. Laser single-photon-ionization mass time-of-flight spectrometry

Reaction products were also analyzed by a SPI-TOF-MS with single-photon-ionization using VUV photons with a wavelength of 118 nm (10.6 eV) (see schematic diagram in Fig. S1 of the SM). The mass spectrometer covers a mass range of *m/z* 10–2000 with mass resolution of 2000 and mass sensitivity of 100 ppm. Mole-fraction calculations were made using propene at *m/z* 42 as a reference (the value measured by gas chromatography at 650 K) [15]. More details about mole fractions calculations can be found in the SM. Products were sampled using a heated quartz capillary tube (200-μm diameter, 5-m length, flow of 3-4 mL/min) directly inserted within the jet-stirred reactor. The whole sampling line was heated to 353 K. This temperature was chosen carefully in order to preserve hydroperoxides and to maximize the related signal.

2.4. cw-Cavity ring down spectroscopy

A tubular-glass *cw*-CRDS cell (length: 76 cm, diameter: 0.8 cm), maintained at a pressure of 1.33 kPa through pumping at both ends has been used to analyze formaldehyde, water, ethylene and hydrogen peroxide in the near infrared at wavelengths in the 6620–6644 cm^{-1} range (more details about experiments and calibration are given in the SM). As described previously [15,19], the cell was coupled to the JSR using a tubular quartz probe with a tip orifice of about 150 μm diameter

The preceding procedure allowed checking the carbon atom balance within a deviation about 10%, except for temperatures close to the maximum of low-temperature reactivity for which larger deviations were spotted (up to 20% at 625 K), certainly due to the condensation of undetected large oxygenated products in GC and SPI-TOF-MS transfer lines. The uncertainty of mole fractions derived from MS measurements is usually estimated as ±10% for major species, ±25% for intermediates with known photo-ionization cross-sections (PICSs), and at least a factor of 2 for those with estimated PICSs. The uncertainty of mole fractions derived from CRDS measurements is usually estimated to be an average of ±15%.

3. Kinetic model development

The 1-hexene oxidation model described hereafter, together with a glossary giving the linear notation corresponding to the name of each species used in the model, can be found in the SM under CHEMKIN format. All the related simulations have been performed using CHEMKIN PRO [20]. This model has been based on the model previously proposed by Bounaceur et al. [8], with some reaction pathways and kinetic data updated according to the recent literature.

3.1. General description of the model of Bounaceur et al. [8]

The model of Bounaceur et al. [8] was generated thanks to software EXGAS which is used to automatically generate models for the oxidation of components of fuels and biofuels [21]. A reaction mechanism generated by EXGAS is made up of three parts:

- A C_0–C_2 reaction base, including all the reactions involving radicals or molecules containing less than three carbon atoms.
- A comprehensive primary mechanism including all the reactions of the molecular reactants, the initial organic compounds and oxygen, and of the derived free radicals.
- A lumped secondary mechanism, containing reactions consuming the molecular products of the primary mechanism which do not react in the reaction base.

Thermochemical data for molecules or radicals are automatically generated based on group and bond additivity methods proposed by Benson [22] using software THERGAS [23].

For alkene low-temperature oxidation, the generic reactions considered in the primary mechanism are:

- "Ene" and "retro-ene" molecular reactions.
- Fuel unimolecular initiations.
- Bimolecular initiations, with O_2 or between two fuel molecules.
- Additions of H atoms and $\dot{O}H$, $\dot{C}H_3$ and $H\dot{O}_2$ (with direct epoxydation) radicals to the fuel double bond.
- The abstraction of alkylic and allylic H-atoms from the fuel molecule.
- The reactions of alkylic, and allylic radicals with oxygen, including the formation of peroxy radicals from alkylic and allylic radicals, as well as the production of dienes and unreactive $H\dot{O}_2$ radicals.
- The radical (alkylic, allylic and peroxy) isomerizations involving a cyclic transition state including a ring with from 4 to 8 members.
- In the case of the peroxy radicals obtained by addition to O_2 of radicals produced by addition of $\dot{O}H$ to the double bond, this pathway includes the Waddington mechanism leading to aldehyde formation [10].