



Measuring hydroperoxide chain-branching agents during *n*-pentane low-temperature oxidation

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Abstract

The reactions of chain-branching agents, such as H₂O₂ and hydroperoxides, have a decisive role in the occurrence of autoignition. The formation of these agents has been investigated in an atmospheric-pressure jet-stirred reactor during the low-temperature oxidation of *n*-pentane (initial fuel mole fraction of 0.01, residence time of 2 s) using three different diagnostics: time-of-flight mass spectrometry combined with tunable synchrotron photoionization, time-of-flight mass spectrometry combined with laser photoionization, and *cw*-cavity ring-down spectroscopy. These three diagnostics enable a combined analysis of H₂O₂, C₁–C₂, and C₃ alkylhydroperoxides, C₃–C₅ alkenylhydroperoxides, and C₅ alkylhydroperoxides including a carbonyl function (keto-hydroperoxides). Results using both types of mass spectrometry are compared for the stoichiometric mixture. Formation data are presented at equivalence ratios from 0.5 to 2 for these peroxides and of two oxygenated products, ketene and pentanediones, which are not usually analyzed during jet-stirred reactor oxidation. The formation of alkenylhydroperoxides during alkane oxidation is followed for the first time. A recently developed model of *n*-pentane oxidation aids discussion of the kinetics of these products and of proposed pathways for C₃–C₅ alkenylhydroperoxides and the pentanediones.

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1. Introduction

The design of advanced-technology engines requires an accurate understanding of fuel autoignition chemistry [1]. It is well known that autoignition is triggered by the reactions of

chain-branching agents such as H_2O_2 or hydroperoxides that are responsible for radical number multiplication [2]. Jet-stirred reactors (JSR) have been shown to be very suitable for studying the chemistry occurring prior to autoignition [3]. Tunable synchrotron vacuum-ultraviolet (SVUV) photoionization mass spectrometry (PIMS) combined with molecular-beam sampling has recently been proven to be a successful method to probe hydroperoxides in JSRs [3,4]. However, these species have not yet been analyzed using a mass-spectrometry method not requiring the use of synchrotron radiation.

The first purpose of this paper is then to present new measurements obtained using a laser-ionization mass spectrometer and to compare them with results obtained using SVUV-PIMS. For the first time, the formation of alkenylhydroperoxides is followed during alkane oxidation. These intermediates have recently been shown to have an important role during the oxidation of alkenes [5], important products of alkane oxidation. The recent SVUV-PIMS analyses during JSR experiments have also enabled detection of oxygenated products that are difficult to quantify by more usual techniques such as gas chromatography [3], notably ketene (rarely quantified in previous JSR studies), and molecules including two carbonyl groups, which we will call diones. The second purpose of this paper is to provide reliable quantification of these products.

The third purpose of this paper is to use *cw*-cavity ring-down spectroscopy (CRDS), another non-synchrotron-based technique, to follow H_2O_2 for a larger fuel. This absolute quantification technique, which requires only the knowledge of the absorption cross-section, has been recently used to probe hydrogen peroxide (H_2O_2) during *n*-butane [3] and dimethylether [6,7] JSR oxidation.

These three objectives are achieved for the oxidation of *n*-pentane for a large range of equivalence ratios (0.5–2); *n*-pentane is a fuel representative of gasoline components for which several recent investigations, including new model development, have been performed [8,9].

2. Experimental facilities

The JSR described below has been associated with three types of analytical tools:

- (1) Molecular-beam sampling into a time-of-flight mass spectrometer combined with SVUV photoionization [10];
- (2) Capillary-tube sampling into a laser single-photon-ionization time-of-flight mass spectrometer;
- (3) Sonic probing into a *cw*-CRDS optical cell using the near-IR wavelength range [12].

The first type of experiments were performed at the National Synchrotron Radiation Labora-

tory (NSRL) in Hefei, China, with gases provided by Nanjing Special Gas Factory Co., Ltd. (purity of +99%) and *n*-pentane provided by Aladdin Reagent Co., Ltd. (purity $\geq 99\%$). The second and third types of measurements were performed at LRGP-Nancy with gases provided by Messer (purity of +99%) and *n*-pentane provided by Sigma-Aldrich (purity $\geq 99\%$). Gas and liquid (prior to vaporization) flows were controlled by mass flow controllers. Dilutants were He in Nancy and Ar in Hefei. The mass-spectrometry and CRDS analyses, including quantification methods, are described in more detail in the Supplementary Material (SM).

2.1. The jet-stirred reactor

As described previously [3,5,7,10–12], the reactor consisted of a quartz sphere (volume $\approx 90 \text{ cm}^3$) in which diluted reactant mixture entered through four turbulent jets. The heated reactor was operated at constant temperature and pressure. A heated quartz annular preheating zone was used to increase gas temperature to the reactor temperature before entering the sphere; gas-mixture residence time inside the preheater was about a few percent of the residence time inside the reactor. Reaction temperature was measured inside the reactor using type K thermocouples, finding temperature gradients always lower than 5 K.

2.2. Molecular-beam sampling and SVUV photoionization mass spectrometry (SVUV-PIMS)

The JSR was coupled with a Hefei lab-made time-of-flight mass spectrometer through a quartz cone-like nozzle, its tip pierced with a 75- μm orifice. A nickel skimmer with a 1.25-mm-diameter aperture was located 15 mm downstream from the sampling nozzle. The SVUV photon beam intersected the molecular beam perpendicularly. Resulting ions were analyzed with a time-of-flight mass spectrometer with mass resolution ($m/\Delta m$) ~ 2000 (see [10,11] for more details). Reactant mole fractions were obtained assuming no reaction below 480 K. For all products apart from carbon oxides and water that were quantified as in [11], mole fractions were calculated at photoionization energy of 11 eV using *n*-pentane signal at m/z 72 and its mole fraction as a reference.

2.3. Capillary-tube sampling with laser single-photon-ionization mass spectrometry (SPI-MS)

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 avoid condensation and also to preserve hydroperoxides, which are fragile due to a

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