An experimental and modelling study of *n*-pentane oxidation in two jet-stirred reactors: The importance of pressure-dependent kinetics and new reaction pathways

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Abstract

Two jet-stirred reactors (JSRs) coupled to gas chromatographic and spectroscopic techniques have been utilised to detect chemical species evolved during *n*-pentane oxidation at 1 and 10 atm, in the temperature range 500–1100 K, and at equivalence ratios of 0.3–2.0. To the authors' knowledge, this is the first study of a fuel's oxidation in *two* JSRs. In addition, the choice of experimental conditions results in there being the same concentration of *n*-pentane in all investigated mixtures; 1% at 1 atm, and 0.1% at 10 atm. This permits the additional assessment of the importance of pressure-dependent kinetics in predicting species concentration profiles. A recently published literature model Bugler et al. (2016) served as the starting point in simulating these experiments, with only minor additions and modifications necessary to achieve good overall agreement. The main adjustments were made to account for multi-oxygenated species (C_5 aldehydes, ketones, diones, *etc.*) detected mainly at low temperatures (<800 K) in both JSRs. In this paper we present new experiments, the most important of which are very well predicted using the aforementioned literature model. The effect of adding chemical pathways, which have been postulated to contribute to the generation of multi-oxygenated species, has been investigated. Finally, a brief account on the importance of pressure-dependent kinetics in the modelling of these experiments is provided.
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1. Introduction

In recent years there has been a renewed interest in understanding the oxidation of alkanes, with a plethora of experimental, theoretical, and

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modelling studies being undertaken by many research groups [1–22]. It is a welcome development that not only are these studies focussing on specific aspects which bolster our overall understanding, but many of these studies take a multi-faceted approach, incorporating these different elements to "tie together" individual efforts and provide greater insights into the complex underlying processes.

This renewed interest may come as no surprise given the ubiquity of alkanes in practical combustion applications. A significant portion of petrol [23], diesel [24], and jet fuels [25] are comprised of alkanes, and their ignition properties, heat release rates, burning velocities, and chemical decomposition pathways need to be well characterised in order to improve the design of the combustors in which they are used. Not only this, but with the advent of kinetically-controlled, low-temperature combustor technologies such as Reactivity Controlled Compression Ignition (RCCI), the chemical characterisation of fuels is now more important than ever [26].

This study represents the latest in a series of collaborative efforts to further our understanding of alkane oxidation [16–18], as well as to refine the fundamental kinetic and thermodynamic parameters which dictate the predictive capabilities of resulting chemical kinetic models. This has been largely aided by the proliferation of theoretical studies in the literature with a focus on accurate determination of these necessary model parameters. The current study builds upon these previous works by incorporating new reaction classes into an *n*-pentane mechanism with the aim of predicting multi-oxygenated species which have only recently become identifiable in experiments. The currently fashionable topic of pressure-dependent kinetics is also explored by taking new, theoretically-derived high-pressure limit rate coefficients and performing an analysis to assess their fall-off from the high-pressure limit. The resulting fall-off rate coefficients are then incorporated into the model to examine their effect.

2. Experimental

2.1. Atmospheric pressure jet-stirred reactor

The JSR experimental setup in Nancy has been used for numerous gas phase kinetic studies of hydrocarbon and oxygenated hydrocarbon fuel oxidation [27]. Experiments were performed at steady state conditions, at a pressure of 1.05 atm, at a residence time of 2 s, at temperatures ranging from 500 to 1100 K, and at three equivalent ratios of 0.5, 1 and 2 with initial fuel mole fractions of 1%. The reactor consists of a fused silica sphere (volume = 81.2 cm^3) into which diluted reactant enters through an injection cross located at its centre. It is operated at constant temperature and pressure

and it is preceded by an annular pre-heating zone in which the temperature of the gases is increased up to the reactor temperature before entering it. Both preheater and reactor were heated to the reaction temperature through the use of Thermocoax resistors with the temperature controlled using type *K* thermocouples (temperature gradients < 5 K). The liquid fuel flow rate was controlled using a Coriolis flow controller, mixed with the carrier gas (helium) and evaporated in a heat exchanger. The fuel was provided by Sigma–Aldrich (purity > 99%). A GC analysis of the fuel reveals a composition of 99.3% *n*-pentane, 0.6% 2-methylbutane, and 0.04% cyclopentane. Helium and oxygen were provided by Messer (purities of 99.99% and 99.999%, respectively). Products have been analyzed online using two complementary methods, namely gas chromatography (GC) and cavity ring-down spectroscopy (CRDS).

Directly connected to the outlet of the reactor, chromatographs were equipped with three columns (carbosphere packed column, PlotQ capillary column, and a HP-5 capillary column), a TCD (thermal conductivity detector) and an FID (flame ionisation detector). A GC–MS operating with electron ionisation (70 eV) was used for products identification. *Cw*-CRDS, a near infrared (6620 ≤ λ ≤ 6644 cm^{-1}) absorption spectroscopic technique was used to analyze water and formaldehyde. A tubular-glass *cw*-CRDS cell (length: 86 cm, diameter: 0.8 cm) working at low pressure (1.33 kPa) was coupled to the reactor through a sonic probe. Mole fractions were calculated using two different absorption lines for each species [28].

2.2. High pressure jet-stirred reactor

The JSR experimental setup at Orléans has been described previously [29]. The experiments were performed at a steady state, at a constant pressure of 10 atm, and a constant mean residence time τ = 0.7 s. The volume of the fused silica spherical reactor was 39 cm^3. The reactants flowed constantly into the JSR and the temperature of the gases inside the reactor was increased stepwise. Uncertainties in reactor temperature, residence time, and reactor pressure are estimated as +/– 3 K, +/– 0.05 s, and +/– 0.1 atm, respectively. Prior to the injectors, they were diluted with nitrogen and mixed. A high degree of dilution (0.1% mol. of fuel) was used to minimize heat release. The reactants were high-purity oxygen (99.995% pure) and high-purity *n*-pentane (>99% pure from Aldrich). They were pre-heated before injection to minimize temperature gradients inside the reactor. A Shimadzu LC10 AD VP pump with an on-line degasser was used to deliver the fuel to an atomizer-vaporizer assembly maintained at 200 °C. Temperature gradients of < 1 K/cm were observed by thermocouple measurements (0.1 mm Pt-Pt/Rh-10%, located inside a thin-wall silica tube). The reacting mixtures were