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A high temperature and atmospheric pressure experimental and detailed chemical kinetic modelling study of 2-methyl furan oxidation

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Abstract

An experimental ignition delay time study for the promising biofuel 2-methyl furan (2MF) was performed at equivalence ratios of 0.5, 1.0 and 2.0 for mixtures of 1% fuel in argon in the temperature range 1200–1800 K at atmospheric pressure. Laminar burning velocities were determined using the heat-flux method for mixtures of 2MF in air at equivalence ratios of 0.55–1.65, initial temperatures of 298–398 K and atmospheric pressure. A detailed chemical kinetic mechanism consisting of 2059 reactions and 391 species has been constructed to describe the oxidation of 2MF and is used to simulate experiment. Accurate reproduction of the experimental data has been obtained over all conditions with the developed mechanism. Rate of production and sensitivity analyses have been carried out to identify important consumption pathways of the fuel and key kinetic parameters under these conditions. The reactions of hydrogen atom with the fuel are highlighted as important under all experimental conditions studied, with abstraction by the hydrogen atom promoting reactivity and hydrogen atom addition to the furan ring inhibiting reactivity. This work, to the authors knowledge, is the first to combine theoretical and experimental work to describe the oxidation of any of the alkylated furans. The mechanism developed herein to describe 2MF combustion should also function as a sub-mechanism to describe the oxidation of 2,5-dimethyl furan whilst also providing key insights into the oxidation of this similar biofuel candidate.

Keywords: 2-Methyl furan; Laminar burning velocity; Ignition delay time; Kinetic modelling; Biofuel

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1. Introduction

The efficient conversion of abundant waste lignocellulosic biomass, not destined for human or animal consumption, into renewable products is a major focus of current research [1–3], as it may offer a means to reduce our reliance on fossil fuel derived products in both the fine chemicals and transportation sectors. Recent developments have focused attention on 2,5-dimethylfuran (25DMF) as a possible alternative transportation fuel, with efficient production via the highly

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versatile platform chemical 5-hydroxymethylfurfural now a possibility [4–7].

25DMF offers significant advantages over the current market leading biofuel, ethanol, in terms of its physicochemical properties as well as its novel production processes. Its energy density (31.5 MJ L^{-1})[8] is greater than ethanol by some 40%, rivaling that of gasoline, with its higher boiling point (366 K) and lower aqueous solubility making it compatible in terms of transportation and storage. Recent engine tests in direct-injection spark-ignition (DISI) engines [9,10] have shown that 25DMF, unlike ethanol, can be burned pure in current internal combustion engines with similar performance to gasoline. Measurements of specific emissions showed carbon monoxide (CO) and hydrocarbon emissions (HC) to be lower than those of gasoline, although greater than those of ethanol. Nitrous oxide and particulate matter emissions were seen to be greater than ethanol and gasoline.

2-methylfuran (2MF) has also very recently entered the fray as a possible alternative biofuel due to the development of novel production methods [11,12]. Engine tests [13] in a DISI engine have been carried out as a result, with comparisons made to conventional research octane number (RON) 95 fuel and ethanol. HC emission reductions of up to 61% were observed when using 2MF as a fuel when compared with RON 95 with efficiency improvements of up to 9.9% observed. Like 25DMF, greater nitrous oxide emissions were measured.

From a chemical kinetic perspective, some of the earliest experimental work on the furans has focused on their pyrolysis. Grela et al. [14] determined the decomposition rates of furan, 2MF and 25DMF in a heated flow reactor at very low pressures (1 mTorr) and temperatures of 1050–1270 K, analysing the final products with on-line mass spectrometry. The presence of carbon monoxide amongst the decomposition products for all three reactant molecules indicated common decomposition pathways.

Similarly, Lifshitz and co-workers [15–17] carried out single pulse shock tube experiments to study the thermal decomposition of furan, 2MF and 25DMF at pressures of 2 atmospheres, in the temperature range 1050–1460 K and residence times of 2 milliseconds, using gas chromatography to analyse the post shock product distributions and developing chemical kinetic mechanisms to rationalise their results. Both Grela et al. and Lifshitz and co-workers found the rate of decomposition of these furans to increase with increasing alkylation of the furan ring. Lifshitz and co-workers also found CO to be a major decomposition product for all three reactants, again indicating similar decomposition channels.

More recent theoretical work has shone light on the decomposition channels of the furans. Sendt et al. [18] used *ab initio* quantum chemical methods and transition state theory to study the thermochemistry and kinetics of the thermal decomposition channels of furan. They found that 1,2-hydrogen atom migrations to form singlet cyclic carbene intermediates were thermochemically and kinetically the most favoured decomposition pathways, concluding that direct ring opening to form either singlet or triplet products was simply too energetic. In a similar work Liu et al. [19,20] reached identical conclusions.

Simmie and Curran [21] employed *ab initio* calculations to determine the formation enthalpies and bond dissociation energies of a range of alkylated furans, including 2MF and 25DMF. They noted the presence of considerably weak carbon–hydrogen bonds on the alkyl side-chain for these species, which readily explains the increasing reactivity observed experimentally by Grela et al. and Lifshitz and co-workers, with increasing alkylation of the furan ring.

Simmie and Metcalfe [22] also used *ab initio* methods to calculate energetics and kinetics of a range of unimolecular decomposition pathways and free radical reactions involving 25DMF, and to a lesser extent 2MF. They concluded, like Sendt et al. and Liu et al., that hydrogen atom migrations to form singlet carbenes play an important role in the decomposition of these species, but the presence of weak C–H bonds in the case of 2MF and 25DMF offers an important site for abstraction by free radicals ($\dot{H}, \dot{O}H, \dot{C}H_3$ etc.) and a key source of reactive hydrogen atoms.

They also rationalise the formation of 2MF from 25DMF, as observed experimentally in flames [23] and shock tubes [17], *via* a $\dot{H}$ atom addition-$\dot{C}H_3$ radical elimination sequence, with a similar process capable of converting 2MF into furan, as observed by Lifshitz and co-workers [16].

Recently, the kinetics of the reaction of 25DMF with hydrogen atoms has been studied by Friese et al. [24] behind reflected shock waves from 970–1240 K and at pressures of 1.6 and 4.8 bar. It was found that the principal pathway proceeds via an addition-elimination mechanism to yield 2MF and methyl radical.

This work will focus on the combustion characteristics of 2MF, a possible biofuel candidate, a known intermediate in the combution of 25DMF and a species whose structural similarities to 25DMF should offer insight into the oxidation pathways of both furanics. This study is believed to be the first to combine experimental work, in the form of ignition delay times and laminar burning velocities, and theoretical work, in the form of a detailed chemical kinetic model, to describe the oxidation of any of these alkylated furans.