



A chemical kinetic study of the reaction of hydroxyl with furans



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HIGHLIGHTS

- Experimental study of the reaction of OH with furan, 2-methyl furan and 2,5-dimethyl furan.
- Hydroxyl radicals measured with high sensitivity and high accuracy using UV absorption.
- 2,5-Dimethyl furan reaction with OH has the highest rate coefficient, followed by 2-methyl furan and furan.
- Experimental rate data are vital for improving prediction of furan kinetic mechanisms.

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ABSTRACT

Furans, a class of cyclic ethers, are potential renewable fuels and additives to conventional fuels. High-temperature oxidation of furans is dominated by their reaction with hydroxyl radical. In this work, rate coefficients for the reaction of hydroxyl (OH) with furan (k_1), 2-methyl furan (k_2) and 2,5-dimethyl furan (k_3) were measured behind reflected shock waves over a temperature range of 890–1388 K and pressures of 1–2 atm. Hydroxyl radicals were generated via the thermal decomposition of tert-butylhydroperoxide. The OH radicals were monitored using the well-characterized R₁(5) rotational line of the A–X (0,0) band in the ultraviolet region near 306 nm. Measurements were carried out under pseudo-first-order conditions using two different mixtures for each furan. The measured rate coefficients can be expressed in Arrhenius form as:

$$k_1 = 783.39 \times T^3 \exp(1866.7/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (924 - 1388 \text{ K})$$

$$k_2 = 8.85 \times 10^{13} \exp(-2285/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (890 - 1333 \text{ K})$$

$$k_3 = 1.03 \times 10^{14} \exp(-2128/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (915 - 1278 \text{ K})$$

This paper presents, to our knowledge, the first high-temperature measurements of the rate coefficients of the reactions of furan and its alkylated derivatives with the OH radical. These data will be critical in improving the predictive capability of chemical kinetic mechanisms of furans.

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1. Introduction

Oxygenated fuels, including alcohols, esters, ethers, aldehydes and furans, are potential renewable fuels and additives to conventional fossil fuels. Furan, and its alkylated derivatives, have

significant advantages over other oxygenated fuels as they can be produced from lignocellulose, which originates from crop, forest and municipal wastes [1–3]. Other oxygenated fuels, such as alcohols, are produced from crops and thus compete with the use of these crops as food. Additionally, the energy density of furans is higher than that of alcohols [2]. A comparison of different methodologies of obtaining oxygenated fuels from biomass can be found in [4]. Furan, and its derivatives, are also found to be important intermediates in the combustion of coal [5]. Investigation of the chemical kinetics of furans is crucial for their efficient use in practical

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combustion devices. Fig. 1 shows the chemical structure of the three cyclic ethers (furans) considered in this study.

Several engine studies have been carried out on furans as fuels or additives to traditional fuels to study engine performance and emission characteristics. A combustion and emissions study of 2,5 DMF in a single cylinder direct injection spark ignition (DISI) engine was carried out by Zhong et al. [6]. An extension to this work has been done by Daniel et al. [7] to compare performance and emissions of 2,5 DMF, ethanol and gasoline. It was shown that 2,5 DMF exhibited comparable combustion characteristics and emissions as gasoline, and in some cases, exceeded ethanol performance. Moreover, they investigated the hydrocarbon and carbonyl (aldehydes and ketones) emissions from a DISI engine for 2,5 DMF, alcohols (methanol, ethanol, n-butanol) and gasoline using gas chromatography, mass spectrometry and high-performance liquid chromatography. The results showed that 2,5 DMF produced the lowest carbonyl emissions compared to other studied fuels [8]. Other engine studies carried out using 2,5 DMF [9] and 2 MF [10] showed that both fuels increased the octane number, and, hence, raised the autoignition resistance.

A number of fundamental kinetic studies have been carried out to understand the chemical kinetic behavior of furans. Pyrolysis of furan, 2-methyl furan (2 MF) and 2,5-dimethyl furan (2,5 DMF) was studied by measuring the products from a heated flow reactor at temperatures ranging 1050–1270 K and low pressures (~ 1 mTorr) [11]. Organ and Mackie [5] studied the pyrolysis of furan behind reflected shock waves over 1100–1700 K and pressure near 20 atm. High-temperature ignition delay times of furan were measured behind reflected shock waves at pressures ranging 1.2–10.4 atm for mixtures with equivalence ratios of 0.5, 1.0, and 2.0 and furan mole fractions of 0.25%, 0.5% and 1% diluted in argon [12]. Tian et al. [13] measured species composition and temperature for a furan/O₂/Ar laminar flame using molecular beam mass spectrometry at low pressures (35 Torr) and equivalence ratios of 1.4, 1.8 and 2.2. Somers et al. [14] measured ignition delay times of 2-methyl furan behind reflected shock waves at atmospheric pressure, temperatures ranging 1200–1800 K and equivalence ratios of 0.5, 1.0 and 2.0. They also measured laminar burning velocities for mixtures of 2 MF in air at equivalence ratios of 0.55–1.65, initial temperatures of 298–398 K and atmospheric pressure. Wei et al. [15] measured ignition delay times of 2 MF/O₂/Ar mixtures at temperatures of 1120–1700 K, pressures of 1.25–10.65 bar and equivalence ratios of 0.25–2.0. For 2,5 DMF, Sirjean et al. [16] measured ignition delay times behind reflected shock waves at different equivalence ratios (0.5–1.5), temperatures of 1300–1831 K and pressures of 1 and 4 bar. Somers et al. [17] presented a comprehensive experimental study for the oxidation and pyrolysis of 2,5 DMF. They measured ignition delay times of DMF/O₂/argon mixtures at atmospheric pressure, temperatures of 1350–1800 K and equivalence ratios of 0.5, 1.0 and 2.0. They also measured ignition delay times for stoichiometric fuel/air mixtures of 2,5 DMF at 20 and 80 bar and temperature ranging 820–1210 K. Additionally, oxidation of 2,5 DMF was studied by Somers et al. [17] with a jet-stirred reactor (JSR) by measuring species concentrations. Somers et al. [17] also measured laminar burning velocities for 2,5 DMF/air mixtures at unburnt gas temperatures of 298 and 358 K. Somers et al. [18] theoretically characterized the pyrolysis of 2 MF using different quantum chemical methods. A recent study by Eldeeb and Akih-Kumgeh [19] compared ignition delay time measurements of furan, 2 MF and 2,5 DMF over 977–1570 K, pressures of 2, 5, 10 and 12 atm and equivalence ratios of 0.5, 1.0 and 2.0. Their results showed that 2 MF is the most reactive fuel followed by furan and 2,5 DMF.

A series of three papers reported experimental data for flat flames of furan [20], 2 MF [21] and 2,5 DMF [22]. Experimental data and kinetic modeling was used to investigate the combustion

chemistry of the three furans. The authors used a combination of high-resolution electron ionization molecular beam mass spectrometry (EI-MBMS) and gas chromatography (GC) to study two low-pressure (20 and 40 mbar) argon-diluted (50%) laminar premixed flat flames at two equivalence ratios ($\phi = 1.0$ and 1.7). Concentrations of reactants, intermediates and products were measured as a function of height above the burner surface. A detailed chemical kinetic model was developed to predict the flame structure of the three furans.

Another very important and fundamental kinetic target, less extensively studied, is the rate coefficient of the reaction of OH with furan, 2 MF and 2,5 DMF.



For furan, 2 MF and 2,5 DMF, the rate coefficients for their reactions with OH were measured at 300 K by [23–25] using a relative kinetic technique. Wine and Thompson [26] measured the rate coefficients for the reaction of OH with furan over a temperature range of 254–425 K using resonance fluorescence spectroscopy. Gómez Alvarez et al. [27] studied the OH-initiated photo-oxidation of furan, 2 MF and 3 MF at atmospheric conditions. The rate coefficients of R1–R3 have also been investigated in various theoretical studies. The rate coefficient of R1 and R2 were theoretically studied using multichannel RRKM-TST, direct-dynamics VTST [28] and by high level theoretical methods [29,30]. In [29], it was shown that the addition channel dominates at low temperatures. Zhang et al. [30,31] calculated the potential energy surface and reaction pathways for R2 and OH + 3 MF reaction. They considered three channels: hydrogen abstraction, bimolecular nucleophilic substitution and OH addition/elimination. Their results revealed that the addition–elimination channel is the dominant one at low to moderately high temperatures. The same conclusion was drawn for room-temperature reaction of OH with various aromatic hydrocarbons including benzene, toluene, xylene isomers and trimethylbenzenes [32].

The focus of the current work is to fill the gap in the high-temperature rate measurements of the reaction of hydroxyl radical with furan, 2 MF and 2,5 DMF. Hydroxyl radicals are generated via thermal decomposition of tert-butyl-hydroperoxide. Rate coefficient measurements are carried out behind reflected shock waves using narrow line-width absorption of OH radical near 306.7 nm.

2. Experiments

All experiments were carried out in the high-purity, honed and electro-polished, stainless steel shock tube facility at King Abdullah University of Science and Technology (KAUST). The shock tube has an inner diameter of 14.2 cm, driven section is 9 m long while the driver section length can be varied to a maximum of 9 m. Five PCB (Model 113B26) piezo-electric pressure transducers (PZT), spaced over the last 1.3 m of the driven section, were used to determine the incident shock velocity ($\pm 0.2\%$). Temperature (T_5) and pressure (P_5) behind reflected shock waves are calculated using standard normal shock relations. Thermochemical data are taken from the Sandia Thermodynamic Database [33] and recent cyclic either mechanism [20–22]. Calculated temperature and pressure have uncertainties of $\pm 0.7\%$ and $\pm 1.0\%$, respectively, primarily due to the uncertainty in the measured incident shock velocity. Christie et al. [34] measured the temperature behind reflected shock waves using quantum cascade laser absorption and showed that the calculated temperatures are within 2–3% of the measured temperatures.

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