A chemical kinetic study of the reaction of hydroxyl with furans

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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-butyl-hydroperoxide. 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:

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

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

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

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.

Keywords: Hydroxyl radical; furan; 2-methyl furan; 2,5-dimethyl furan; shock tube; laser absorption

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 combustion devices. Figure 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 to 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 to 1700 K, pressures of 1.25 to 10.65 bar and equivalence ratios of 0.25 to 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 to 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. Gomez 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 meters 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 ether 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.

Chrystie 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. A turbo-molecular pump (Varian TV 551) was used to pump down the driven section of the shock tube for about 30 minutes between two successive experiments and an ultimate pressure of 2×10^{-5} mbar was achieved without-gassing leak rate of 5×10^{-6} mbar/min. Further details of the shock tube facility can be found elsewhere [34-36].

Test gas mixtures were prepared using research-grade argon (99.999%), 70% TBHP (tert-butyl-hydroperoxide) aqueous solution and furan ($\geq 99\%$), 2 MF (99%) or 2,5 DMF (99%). Argon was supplied by Abdullah Hashim Gases (AHG) and other chemicals were procured from Sigma Aldrich. TBHP is a well-known thermal precursor of OH radicals [37]. A comparison between TBHP and gaseous nitric acid as OH precursors can be found in [37, 38]. Repeated freeze-pump-thaw cycles were used to further purify the furans before preparing the gas mixtures. High-purity helium (99.99%), supplied by AHG, was used as the driver gas.

Temporal OH radical concentration was measured behind reflected shock waves using the well-characterized $R_1(5)$ absorption line of the OH A–X (0, 0) band near 306.69 nm. A 532 nm (10 W, cw) green laser pumped a Rhodamine B dye-laser (0.75 g/L Rhodamine B in ethylene glycol) to generate visible red light near 613.4 nm (~ 1 W). The red light was frequency doubled to generate ultraviolet light (~ 100 mW) near 306.7 nm. A common-mode-rejection scheme was used to minimize the noise to signal ratio (see Figure 1 in [35]). Hydroxyl radical mole fraction (X_{OH}) was calculated using the Beer-Lambert law, $I/I_0 = \exp(-k_v X_{OH} P_5 L)$, where I and I_0 are the transmitted and incident laser intensities, respectively, k_v is the absorption coefficient calculated following the work of Herbon [39], P_5 is the total reflected shock pressure (atm) and L is the optical path length (14.2 cm). The overall estimated uncertainty in the measured OH mole fraction is approximately $\pm 5\%$, mainly due to the uncertainties in the

reflected-shock temperature and absorption coefficient. All experimental data were recorded at 2.5 MHz sampling rate using a high-resolution (14 bit) data acquisition system.

3. Results

Hydroxyl radical profiles are simulated with a chemical kinetic mechanism and the target rate (fuel + OH) is varied until a best fit is achieved with the measured OH mole fraction profile. Detailed kinetic mechanism developed by Kohse-Höinghaus et al. [20-22] for furan, 2 MF and 2,5 DMF is used as the base mechanism. A TBHP ((CH₃)₃CO-OH) chemistry set, described in [40-43], is included in the base mechanism to simulate the formation of OH. Following Benson and O'Neal [44], TBHP decomposes almost instantaneously to form the OH radical and a tert-butoxy radical, which in turn decomposes to form acetone and a methyl radical. Moreover, the OH radical can attack TBHP to produce water and other products [41-43]. The rate coefficients of the TBHP relevant reactions and thermodynamic properties of the newly introduced species are taken as described in Lam et al. [40]. All zero-dimensional simulations are performed using CHEMKIN-PRO [45] software package with constant volume and energy constraints (constant UV). Measurements are performed under pseudo-first-order conditions by having fuel (furan, 2 MF or 2,5 DMF) concentrations to be at least ten times larger than OH concentration. The rate coefficients for reactions of R1 – R3 are measured behind reflected shock waves over a temperature range of 890 – 1388 K and pressures ranging 1.05 – 1.95 atm.

3.1. Kinetics of furan + OH

A representative hydroxyl radical sensitivity analysis is shown in Fig. 2 for a mixture of 228 ppm furan with 11 ppm TBHP (and 30 ppm H₂O) diluted in argon. Reflected shock conditions are 1015 K and 1.56 atm. The OH sensitivity is calculated as $S = (\partial X_{OH} / \partial k_i) \times (k_i / X_{OH})$, where X_{OH} is the OH mole fraction and k_i is the rate coefficient of the i^{th} reaction.

Sensitivity analysis shown in Fig. 2 shows that the reaction of furan with OH (R1) is the dominant reaction over the entire time frame of the experiments (~ 200 μ s). For low temperatures and at early times (< 10 μ s), minor interference from the decomposition reaction of TBHP is seen. However, the influence of this interference on the OH radical decay and on the deduced reaction rate is negligible. At longer times (> 200 μ s), secondary reactions, such as the following, start to show some interference.

The rate coefficient of reaction R4 was updated in the base mechanism with the measured values proposed by Pang et al. [46]. The rate coefficient of reaction R5 was updated as measured by Oehlschlaeger et al. [47], while the rate coefficient for reaction R6 was updated with the measured values from Lam et al. [40]. Finally, the rate coefficient of reaction R7 was updated with the values measured by Srinivasan et al. [48].

A representative measured OH mole fraction profile for a mixture of 228 ppm furan/11 ppm TBHP/30 ppm water diluted in argon is shown in Fig. 3 at reflected shock temperature and pressure of at 1015 K and 1.56 atm, respectively. The best-fit rate coefficient for R1 and perturbations of $\pm 20\%$ in the inferred rate coefficient are also presented in Fig. 3. Time zero is determined by matching the peak of simulated OH profile with the measured OH peak. The experimental slow rise of OH radical before $t = 0$ (for temperatures > 1000 K) is attributed to the relatively low bandwidth (760 kHz) of the photo-detector. The detector bandwidth can be set as high as 10 GHz but the signal-to-noise-ratio is lower at higher bandwidth. At lower temperatures (<1000 K), the experimental slow rise of OH disappears because the detector bandwidth is high enough to capture the rise of OH fairly well. Figure 3 shows a notch, Schlieren spike, in the measured trace close to the peak, which is caused by the shock-induced density gradient. Table

1 summarizes the rate coefficient measurements of reaction R1 over a temperature range of 924 – 1388 K and pressures of 1.17 – 1.95 atm. Rate coefficient measurements were performed using two separate mixtures (see Table 1 and Fig. 5) to check if the mixture composition affected the measured rates. The measured rate coefficients are found to be independent of the mixture composition or fuel concentration for the range of conditions studied here.

Detailed error analysis was performed to estimate the overall uncertainty in the measured rate coefficients of reaction R1 at representative condition of 1015 K and 1.56 atm. The individual sources of errors considered in this study include the temperature ($\pm 1\%$), mixture composition ($\pm 5\%$), OH absorption coefficient ($\pm 3\%$), wavemeter reading ($\pm 0.002 \text{ cm}^{-1}$), fitting the experimental profiles ($\pm 5\%$), locating time zero ($\pm 1 \text{ }\mu\text{s}$), rate coefficient of $\text{CH}_3 + \text{OH} = \text{S-CH}_2 + \text{H}_2\text{O}$ (uncertainty factor = 2), rate coefficient of $\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$ ($\pm 20\%$), rate coefficient of $\text{CH}_3\text{COCH}_3 + \text{OH} = \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$ (+17%, -28%) and the rate coefficient of $\text{CH}_3\text{OH} = \text{CH}_3 + \text{OH}$ (uncertainty factor = 2). The contribution of each of these error sources on the determination of k_1 is calculated separately and presented in Fig. 4. The overall uncertainty is calculated using the root-sum-squared method and is found to be +15% / -20% for k_1 at 1015 K.

The measured rate coefficients for reaction R1 (furan + OH) are plotted in Fig. 5 over a temperature range of 924 – 1388 K. The values adopted in the kinetic mechanism of Liu et al. [20] are also shown and agree quite well with the current measurements. The measured rate coefficients can be expressed in a modified Arrhenius form as:

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

The measurements, and adopted values of Liu et al. [20], exhibit a slight non-Arrhenius curvature over the temperature range of this study. Also, the activation energy of the reaction is relatively small over this temperature range. It can be argued that the reaction of hydroxyl with furan predominantly follows addition-elimination pathway than direct H-abstraction.

3.2. Kinetics of 2-methyl furan + OH

The overall rate coefficients of the reaction of 2-methyl furan (2 MF) with OH were measured behind reflected shock waves over a temperature range of 890 – 1333 K and pressures near 1 – 1.5 atm. Similar to the furan + OH case, two test mixtures were used: 258 ppm 2 MF/12 ppm TBHP/32 ppm H₂O diluted in argon and 153 ppm 2 MF/13 ppm TBHP/34 ppm H₂O diluted in argon. The OH sensitivity analysis for the second mixture is shown in Fig. 6 at reflected shock conditions of 1150 K and 1.43 atm. The dominant reaction is R2 (2 MF + OH → Products) while the primary interfering reactions are R4 – R7. The rate coefficients for these reactions were updated in the base mechanism, as discussed earlier.

Figure 7 shows a representative measured OH temporal profile at 1150 K and 1.43 atm. The best-fit simulated OH profile and perturbations of ± 20 % in the inferred rate coefficient are also shown in Fig. 7. A more noticeable Schlieren spike is seen in Fig. 7 compared to Fig. 3. The higher temperature case shown in Fig. 7 causes relatively large density change which results in a larger Schlieren spike. Rate coefficients of reaction R2, measured over 890 – 1327 K, are presented in Table 2 and plotted in Fig. 8. Two different mixture compositions were employed to confirm the independency of the rate coefficients on secondary chemistry effects. Rate coefficient values adopted in the kinetic mechanisms of Tran et al. [21] and Sirjean et al. [16] are also shown in Fig. 8. Both mechanisms have employed identical Arrhenius expression for k_2 . The predicted rate coefficients are approximately 50% slower than the current measurements for temperatures less than 1150 K, while the predictions agree well with current measurements for higher temperatures ($T \geq 1300$ K). The values of the measured rate coefficient can be expressed in Arrhenius form as:

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

Detailed error analysis was performed for k_2 measurements in a manner analogous to that described for k_1 . The overall uncertainty in the measured rate coefficient of reaction R2 comes out to be +17% / -21% at 1150 K.

3.3. Kinetics of 2,5-dimethyl furan + OH

Following the same procedure of measuring rate coefficients of reactions R1 and R2, the overall rate coefficients of the reaction of 2,5-dimethyl furan (2,5 DMF) with OH were measured behind reflected shock waves for a temperature range of 915 – 1278 K and pressures near 1.2 – 1.7 atm. To investigate any potential interference from secondary reactions, two test mixtures were used: 250 ppm 2,5 DMF/16 ppm TBHP/38 ppm H₂O in argon and 191 ppm 2,5 DMF/14 ppm TBHP/34 ppm H₂O in argon. Figure 9 shows representative sensitivity analysis for the second mixture at reflected shock conditions of 1251 K and 1.28 atm. It can be seen that the target reaction R3 is dominant for the first 70 μ s and then the sensitivity to R3 decreases with an increase in interference from CH₃ + OH (R4). Therefore, we have only used the first 50 – 70 μ s of the measured OH profiles to deduce k_3 .

A representative measured OH time-history profile is shown in Fig. 10 at 1251 K and 1.28 atm. The TBHP chemistry set is added to the chemical kinetic mechanism of Togbé et al. [22] to simulate the OH profiles. The best-fit simulated OH profile and perturbations of $\pm 20\%$ in the inferred rate coefficient are shown in Fig. 10. Rate coefficients of reaction R3, measured over 915 – 1278 K, are presented in Table 3 and plotted in Fig. 11. Rate coefficient values adopted in mechanisms of Togbé et al. [22], Sirjean et al. [16] and Somers et al. [17] are also shown in Fig. 11. The values of k_3 from Togbé et al. [22] and Sirjean et al. [16] are equal and approximately two times larger than the current measurements. However, the activation energy predicted by these models is quite similar to the activation energy of the measurements. Predicted values of k_3 by Somers et al. [17] show larger curvature and are even higher than the other two

mechanisms. The values of the measured rate coefficient can be expressed in the Arrhenius form as:

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

Similar to the methodology used for k_1 , detailed error analysis was performed to estimate the uncertainty in k_3 and the uncertainty is found to be +17% / -22% at 1251 K.

The presence of the methyl group in the ring side affects the rate coefficients of the reaction of hydroxyl with alkylated derivatives of furan, as can be seen in Fig. 12. The rate coefficients of the reaction of 2,5 DMF with OH are approximately two times higher than those of 2 MF with OH. This can be attributed to the fact that 2,5 DMF has two methyl groups while 2 MF has only one. This variation of the measured total rate coefficients with number of methyl groups and the Arrhenius nature of the rate coefficients suggests that, in our T range, H-abstraction from the methyl groups is comparable to or faster than competing pathways via addition of OH to the furan ring. A direct measurement of the product branching ratio would be very helpful.

Our measured high-temperature rate coefficients are compared with low-temperature ($T < 500$ K) literature data in Figure S1 (Supplementary Material). The low-temperature data for all three furans are higher than the corresponding measurements at high temperatures. This indicates that OH-addition pathways dominate for these furans at low temperatures.

4. Conclusions

The overall rate coefficients for the reaction of OH radical with furan (k_1), 2-methyl furan (k_2) and 2,5-dimethyl furan (k_3) are reported over a temperature range of 890 – 1388 K and pressures near 1 – 2 atm. The rate coefficients of 2,5 DMF + OH reaction are the largest followed by 2 MF + OH. The rate coefficients of furan + OH are smallest and show slight curvature over the measured temperature range. Our high-temperature measurements are smaller compared to the literature rate coefficient data at temperatures near 300 K. This indicates that OH-addition pathways dominate for these cyclic ethers at low temperatures. The reported measurements represent, to our knowledge, the first high-temperature rate coefficient data for these cyclic ethers. Direct measurements of product branching ratios will be useful in determining the branching of direct abstraction and addition pathways at intermediate to high temperatures.

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TABLES

Table 1. Rate coefficient data for furan + OH reaction.

T_5 [K]	P_5 [atm]	k_1 [$\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$]
228 ppm furan with 11 ppm TBHP / 30 ppm H_2O in Ar		
924	1.43	5.15E+12
991	1.37	5.19E+12
1000	1.56	5.25E+12
1015	1.56	5.22E+12
1046	1.51	5.35E+12
1135	1.38	5.67E+12
1176	1.95	5.76E+12
1188	1.77	5.98E+12
1197	1.57	5.95E+12
1224	1.43	6.24E+12
167 ppm furan with 13 ppm TBHP / 36 ppm H_2O in Ar		
1170	1.31	6.11E+12
1250	1.4	6.67E+12
1270	1.25	7.14E+12
1272	1.25	6.76E+12
1286	1.41	7.09E+12
1286	1.17	7.22E+12
1305	1.22	7.65E+12
1380	1.38	8.59E+12
1388	1.39	8.15E+12

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Table 3. Rate rate coefficient data for 2,5 DMF + OH reaction.

T_5 [K]	P_5 [atm]	k_3 [cm ³ mol ⁻¹ s ⁻¹]
250 ppm 2,5 DMF with 16 ppm TBHP / 38 ppm H ₂ O in Ar		
915	1.56	9.55E+12
930	1.74	1.06E+13
1000	1.45	1.28E+13
1064	1.44	1.33E+13
1078	1.32	1.36E+13
1103	1.66	1.50E+13
191 ppm 2,5 DMF with 13 ppm TBHP / 34 ppm H ₂ O in Ar		
1134	1.35	1.57E+13
1204	1.38	1.75E+13
1223	1.23	1.79E+13
1246	1.35	1.85E+13
1246	1.19	2.00E+13
1251	1.28	1.83E+13
1278	1.33	1.87E+13

FIGURES

Figure 1. Chemical structures of furan, 2-methyl furan (2 MF) and 2,5-dimethyl furan (2,5 DMF).

Figure 2. Hydroxyl radical sensitivity for the rate coefficient measurement of R1 (furan + OH).

Figure 3. A representative measured OH temporal profile for the rate coefficient of furan + OH. Best-fit simulated rate coefficient and perturbations of $\pm 20\%$ are also shown. Simulations are performed using the Liu et al.[\[20\]](#) kinetic mechanism.

Figure 4. Uncertainty analysis for the rate coefficient of furan + OH reaction at the conditions of Fig. 3.

Figure 5. Arrhenius plot of measured rate coefficients for furan + OH reaction (k_1). Prediction from Liu et al.[\[20\]](#) mechanism are also shown. Measurements were performed using two different mixtures, as indicated, and the results are independent of the mixture composition.

Figure 6. Hydroxyl radical sensitivity for the rate constant measurement of R2 (2 MF + OH $\rightarrow$ Products).

Figure 7. A representative measured OH temporal profile for measurements of the rate coefficient of 2-MF + OH. Best-fit simulated rate coefficient and perturbations of $\pm 20\%$ are also shown. Simulations are performed using the Tran et al.[\[21\]](#) mechanism.

Figure 8. Arrhenius plot of measured rate coefficients for 2 MF + OH reaction (k_1). Predicted values from Sirjean et al.[16] and Tran et al.[21] mechanisms are also shown. Measurements were performed using two different mixtures, as indicated, and the results are found to be independent of the mixture composition.

Figure 9. Hydroxyl sensitivity for the rate constant measurement of R3 at 1251 K and 1.28 atm.

Figure 10. A representative measured OH mole fraction profile for measuring the rate coefficient of 2,5 DMF + OH at 1251 K and 1.28 atm. Best-fit simulated rate coefficient and perturbations of $\pm 20\%$ are also shown. Simulations are performed using the Togbé et al.[\[22\]](#) mechanism.

Figure 11. Arrhenius plot for 2,5 DMF + OH (k_3). Rate coefficients adopted in the mechanisms of Togbé et al.[\[22\]](#), Sirjean et al.[\[16\]](#) and Somers et al.[\[17\]](#) are also shown.

Figure 12. Comparison of the overall rate coefficients.

Supplementary Material

Figure S1: Comparison of current high-temperature measurements with low-temperature literature data

429 References

- 430 [1] F. Cherubini, A.H. Strømman, Chemicals from lignocellulosic biomass: opportunities, perspectives,
431 and potential of biorefinery systems, *Biofuels, Bioproducts and Biorefining*, 5 (2011) 548-561.
- 432 [2] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Production of dimethylfuran for liquid fuels
433 from biomass-derived carbohydrates, *Nature*, 447 (2007) 982-985.
- 434 [3] W. Yang, A. Sen, One-Step Catalytic Transformation of Carbohydrates and Cellulosic Biomass to 2, 5-
435 Dimethyltetrahydrofuran for Liquid Fuels, *ChemSusChem*, 3 (2010) 597-603.
- 436 [4] L.S. Tran, B. Sirjean, P.-A. Glaude, R. Fournet, F. Battin-Leclerc, Progress in detailed kinetic modeling
437 of the combustion of oxygenated components of biofuels, *Energy*, 43 (2012) 4-18.
- 438 [5] P.P. Organ, J.C. Mackie, Kinetics of pyrolysis of furan, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 815-
439 823.
- 440 [6] S. Zhong, R. Daniel, H. Xu, J. Zhang, D. Turner, M.L. Wyszynski, P. Richards, Combustion and emissions
441 of 2, 5-dimethylfuran in a direct-injection spark-ignition engine, *Energy & Fuels*, 24 (2010) 2891-2899.
- 442 [7] R. Daniel, G. Tian, H. Xu, M.L. Wyszynski, X. Wu, Z. Huang, Effect of spark timing and load on a DISI
443 engine fuelled with 2, 5-dimethylfuran, *Fuel*, 90 (2011) 449-458.
- 444 [8] R. Daniel, L. Wei, H. Xu, C. Wang, M.L. Wyszynski, S. Shuai, Speciation of hydrocarbon and carbonyl
445 emissions of 2, 5-dimethylfuran combustion in a DISI engine, *Energy & Fuels*, 26 (2012) 6661-6668.
- 446 [9] D.A. Rothamer, J.H. Jennings, Study of the knocking propensity of 2, 5-dimethylfuran–gasoline and
447 ethanol–gasoline blends, *Fuel*, 98 (2012) 203-212.
- 448 [10] M. Thewes, M. Muether, S. Pischinger, M. Budde, A. Brunn, A. Sehr, P. Adomeit, J. Klankermayer,
449 Analysis of the impact of 2-methylfuran on mixture formation and combustion in a direct-injection
450 spark-ignition engine, *Energy & Fuels*, 25 (2011) 5549-5561.
- 451 [11] M. Grela, V. Amorebieta, A. Colussi, Very low pressure pyrolysis of furan, 2-methylfuran and 2, 5-
452 dimethylfuran. The stability of the furan ring, *The Journal of Physical Chemistry*, 89 (1985) 38-41.
- 453 [12] L. Wei, C. Tang, X. Man, X. Jiang, Z. Huang, High-temperature ignition delay times and kinetic study
454 of furan, *Energy & Fuels*, 26 (2012) 2075-2081.
- 455 [13] Z. Tian, T. Yuan, R. Fournet, P.-A. Glaude, B. Sirjean, F. Battin-Leclerc, K. Zhang, F. Qi, An
456 experimental and kinetic investigation of premixed furan/oxygen/argon flames, *Combustion and flame*,
457 158 (2011) 756-773.
- 458 [14] K.P. Somers, J.M. Simmie, F. Gillespie, U. Burke, J. Connolly, W.K. Metcalfe, F. Battin-Leclerc, P.
459 Dirrenberger, O. Herbinet, P.-A. Glaude, A high temperature and atmospheric pressure experimental
460 and detailed chemical kinetic modelling study of 2-methyl furan oxidation, *Proceedings of the*
461 *Combustion Institute*, 34 (2013) 225-232.
- 462 [15] L. Wei, C. Tang, X. Man, Z. Huang, Shock-Tube Experiments and Kinetic Modeling of 2-Methylfuran
463 Ignition at Elevated Pressure, *Energy & Fuels*, 27 (2013) 7809-7816.
- 464 [16] B. Sirjean, R. Fournet, P.-A. Glaude, F. Battin-Leclerc, W. Wang, M.A. Oehlschlaeger, Shock tube and
465 chemical kinetic modeling study of the oxidation of 2, 5-dimethylfuran, *The Journal of Physical*
466 *Chemistry A*, 117 (2013) 1371-1392.
- 467 [17] K.P. Somers, J.M. Simmie, F. Gillespie, C. Conroy, G. Black, W.K. Metcalfe, F. Battin-Leclerc, P.
468 Dirrenberger, O. Herbinet, P.-A. Glaude, A comprehensive experimental and detailed chemical kinetic
469 modelling study of 2, 5-dimethylfuran pyrolysis and oxidation, *Combustion and flame*, 160 (2013) 2291-
470 2318.
- 471 [18] K.P. Somers, J.M. Simmie, W.K. Metcalfe, H.J. Curran, The pyrolysis of 2-methylfuran: a quantum
472 chemical, statistical rate theory and kinetic modelling study, *Phys. Chem. Chem. Phys.*, 16 (2014) 5349-
473 5367.

474 [19] M.A. Eldeeb, B. Akih-Kumgeh, Reactivity trends in furan and alkyl furan combustion, *Energy & Fuels*,
 475 28 (2014) 6618-6626.

476 [20] D. Liu, C. Togbé, L.-S. Tran, D. Felsmann, P. Oßwald, P. Nau, J. Koppmann, A. Lackner, P.-A. Glaude,
 477 B. Sirjean, Combustion chemistry and flame structure of furan group biofuels using molecular-beam
 478 mass spectrometry and gas chromatography–Part I: Furan, Combustion and flame, 161 (2014) 748-765.

479 [21] L.-S. Tran, C. Togbé, D. Liu, D. Felsmann, P. Oßwald, P.-A. Glaude, R. Fournet, B. Sirjean, F. Battin-
 480 Leclerc, K. Kohse-Höinghaus, Combustion chemistry and flame structure of furan group biofuels using
 481 molecular-beam mass spectrometry and gas chromatography–Part II: 2-Methylfuran, Combustion and
 482 flame, 161 (2014) 766-779.

483 [22] C. Togbé, L.-S. Tran, D. Liu, D. Felsmann, P. Oßwald, P.-A. Glaude, B. Sirjean, R. Fournet, F. Battin-
 484 Leclerc, K. Kohse-Höinghaus, Combustion chemistry and flame structure of furan group biofuels using
 485 molecular-beam mass spectrometry and gas chromatography–Part III: 2, 5-Dimethylfuran, Combustion
 486 and flame, 161 (2014) 780-797.

487 [23] A. Bierbach, I. Barnes, K. Becker, Rate coefficients for the gas-phase reactions of hydroxyl radicals
 488 with furan, 2-methylfuran, 2-ethylfuran and 2, 5-dimethylfuran at 300±2 K, *Atmospheric Environment*.
 489 Part A. General Topics, 26 (1992) 813-817.

490 [24] S.M. Aschmann, N. Nishino, J. Arey, R. Atkinson, Kinetics of the Reactions of OH Radicals with 2-and
 491 3-Methylfuran, 2, 3-and 2, 5-Dimethylfuran, and E-and Z-3-Hexene-2, 5-dione, and Products of OH+ 2, 5-
 492 Dimethylfuran, *Environ. Sci. Technol.*, 45 (2011) 1859-1865.

493 [25] S.M. Aschmann, N. Nishino, J. Arey, R. Atkinson, Products of the OH Radical-Initiated Reactions of
 494 Furan, 2-and 3-Methylfuran, and 2, 3-and 2, 5-Dimethylfuran in the Presence of NO, *The Journal of*
 495 *Physical Chemistry A*, 118 (2013) 457-466.

496 [26] P. Wine, R. Thompson, Kinetics of OH reactions with furan, thiophene, and tetrahydrothiophene,
 497 *International journal of chemical kinetics*, 16 (1984) 867-878.

498 [27] E. Gómez Alvarez, E. Borrás, J. Viidanoja, J. Hjorth, Unsaturated dicarbonyl products from the OH-
 499 initiated photo-oxidation of furan, 2-methylfuran and 3-methylfuran, *Atmos. Environ.*, 43 (2009) 1603-
 500 1612.

501 [28] S.H. Mousavipour, S. Ramazani, Z. Shahkolahi, Multichannel RRKM-TST and Direct-Dynamics VTST
 502 Study of the Reaction of Hydroxyl Radical with Furan, *The Journal of Physical Chemistry A*, 113 (2009)
 503 2838-2846.

504 [29] J.M. Anglada Rull, The Gas Phase HO-Initiated Oxidation of Furan: A Theoretical Investigation on the
 505 Reaction Mechanism, *Open Chemical Physics Journal*, 1 (2008) 80-93.

506 [30] W. Zhang, B. Du, L. Mu, C. Feng, Computational study on the mechanism for the reaction of OH with
 507 2-methylfuran, *Journal of Molecular Structure: THEOCHEM*, 851 (2008) 353-357.

508 [31] W. Zhang, B. Du, L. Mu, C. Feng, Mechanism for the gas-phase reaction between OH and 3-
 509 methylfuran: A theoretical study, *International Journal of Quantum Chemistry*, 108 (2008) 1232-1238.

510 [32] D.A. Hansen, R. Atkinson, J.N. Pitts, Rate constants for the reaction of hydroxyl radicals with a series
 511 of aromatic hydrocarbons, *The Journal of Physical Chemistry*, 79 (1975) 1763-1766.

512 [33] R. Kee, F. Rupley, J. Miller, The Chemical Thermodynamic Data Base, Report No, SAND87-8215B.
 513 UC-4, Sandia National Laboratory, (1987).

514 [34] R.S. Chrystie, E.F. Nasir, A. Farooq, Towards simultaneous calibration-free and ultra-fast sensing of
 515 temperature and species in the intrapulse mode, *Proceedings of the Combustion Institute*, 35 (2015)
 516 3757-3764.

517 [35] J. Badra, A.E. Elwardany, F. Khaled, S.S. Vasu, A. Farooq, A shock tube and laser absorption study of
 518 ignition delay times and OH reaction rates of ketones: 2-Butanone and 3-buten-2-one, *Combustion and*
 519 *Flame*, 161 (2014) 725-734.

520 [36] A. Elwardany, E. Nasir, E. Es-sebbar, A. Farooq, Unimolecular decomposition of formic and acetic
 521 acids: A shock tube/laser absorption study, *Proceedings of the Combustion Institute*, (2014).

- [37] V. Vasudevan, D.F. Davidson, R.K. Hanson, High-temperature measurements of the reactions of OH with toluene and acetone, *The Journal of Physical Chemistry A*, 109 (2005) 3352-3359.
- [38] T. Seta, M. Nakajima, A. Miyoshi, High-temperature reactions of OH radicals with benzene and toluene, *The Journal of Physical Chemistry A*, 110 (2006) 5081-5090.
- [39] J.T. Herbon, Shock tube measurements of $\text{CH}_3 + \text{O}_2$ kinetics and the heat of formation of the OH radical, in, Stanford University, 2004.
- [40] K.-Y. Lam, D.F. Davidson, R.K. Hanson, High-Temperature Measurements of the Reactions of OH with a Series of Ketones: Acetone, 2-Butanone, 3-Pentanone, and 2-Pentanone, *The Journal of Physical Chemistry A*, 116 (2012) 5549-5559.
- [41] J. Badra, A.E. Elwardany, F. Khaled, S.S. Vasu, A. Farooq, A shock tube and laser absorption study of ignition delay times and OH reaction rates of ketones: 2-Butanone and 3-buten-2-one, *Combust. Flame*, (2013).
- [42] S.S. Vasu, J. Zádor, D.F. Davidson, R.K. Hanson, D.M. Golden, J.A. Miller, High-Temperature Measurements and a Theoretical Study of the Reaction of OH with 1, 3-butadiene, *The Journal of Physical Chemistry A*, 114 (2010) 8312-8318.
- [43] S.S. Vasu, Z. Hong, D.F. Davidson, R.K. Hanson, D.M. Golden, Shock tube/laser absorption measurements of the reaction rates of OH with ethylene and propene, *J. Phys. Chem. A*, 114 (2010) 11529-11537.
- [44] S.W. Benson, H.E. O'Neal, Kinetic data on gas phase unimolecular reactions, in, DTIC Document, 1970.
- [45] R. Kee, F. Rupley, J. Miller, M. Coltrin, J. Grcar, E. Meeks, H. Moffat, A. Lutz, G. Dixon-Lewis, M. Smooke, CHEMKIN-PRO, Release 15105, in, Reaction Design, Inc.: San Diego, CA, 2010.
- [46] G.A. Pang, R.K. Hanson, D.M. Golden, C.T. Bowman, High-Temperature Measurements of the Rate Constants for Reactions of OH with a Series of Large Normal Alkanes: n-Pentane, n-Heptane, and n-Nonane, *Z. Phys. Chem.*, 225 (2011) 1157-1178.
- [47] M.A. Oehlschlaeger, D.F. Davidson, R.K. Hanson, High-temperature ethane and propane decomposition, *Proc. Combust. Inst.*, 30 (2005) 1119-1127.
- [48] N. Srinivasan, M.-C. Su, J. Michael, High-Temperature Rate Constants for $\text{CH}_3\text{OH} + \text{Kr} \rightarrow \text{Products}$, $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{Products}$, $\text{OH} + (\text{CH}_3)_2\text{CO} \rightarrow \text{CH}_2\text{COCH}_3 + \text{H}_2\text{O}$, and $\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$, *The Journal of Physical Chemistry A*, 111 (2007) 3951-3958.