

Kinetic Investigation of the Reactions of 2,5-Dimethylfuran and 2-Methylfuran with Hydroxyl Radicals

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Abstract

The rate coefficients for the reactions of 2,5-dimethylfuran (DMF) + OH and 2-methylfuran (MF) + OH were experimentally determined in a slow-flow reactor in a pressure range of 7–21 bar (helium as bathgas). The OH radicals were produced by laser flash-photolysis of nitric acid and detected time-resolved by laser induced fluorescence. The rate coefficients determined show a non-Arrhenius temperature dependence; two different regimes can be distinguished. In the first regime the temperature dependence can be described by the following Arrhenius expressions: $k_{\text{OH+DMF}} = (3.38 \pm 1.0) \times 10^{-11} \exp(219 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1}$ ($T = 295\text{--}350 \text{ K}$, $P = 7\text{--}21 \text{ bar}$) and $k_{\text{OH+MF}} = (1.23 \pm 0.37) \times 10^{-11} \exp(500 \text{ K}/T) \text{ cm}^3 \text{ s}^{-1}$ ($T = 295\text{--}350 \text{ K}$, $P = 13\text{--}21 \text{ bar}$). Above 350 K a much more pronounced decrease of the rate coefficient with temperature was found. The overall behavior may be explained by non-reversible addition of the OH radical in the first regime and reversible addition in the second regime.

Introduction

Diminishing fossil fuel reserves and growing concerns about global warming indicate that sustainable energy sources are increasingly needed. A promising biofuel candidate is 2,5-dimethylfuran (DMF), which can be produced from biomass, in particular from crops not destined for human nutrition, *via* catalytic routes [1]. Compared to ethanol, which is currently the most widely used biofuel, DMF has several advantages as *e. g.* a larger energy density, a higher boiling point and its low solubility in water [2].

DMF and 2-methylfuran (MF) are directly emitted into the atmosphere from incomplete combustion of fossil fuels, waste and, in particular, from biomass burning [3]. Furthermore, furan derivatives are known to be produced during photooxidation of hydrocarbons [4]. In the atmosphere, their chemical degradation is mainly initiated by reaction with OH radicals. Moreover, fuel + OH reactions are of particular importance in low-temperature combustion.

Bierbach *et al.* [5] and Aschmann *et al.* [6] have already published experimental studies for the reactions of DMF + OH and MF + OH. Both groups of authors determined the rate coefficients at room temperature and around 1 bar using a relative rate method. The temperature dependence was not measured.

Moreover, Zhang *et al.* [7] carried out quantum chemical calculations on the reaction of OH with MF using several compound methods. They characterized two kinds of reaction pathways including the direct hydrogen abstraction channels and the association channels forming 2-methylfuran-OH adduct. The potential energy surface indicates that an addition mechanism to the double bond is likely for this reaction, and a negative temperature dependence of the rate coefficient is predicted.

In this work, we report on experiments at 295–560 K for DMF + OH and 295–410 K for MF + OH in a pressure range of 7–21 bar. We discuss mechanistic

aspects and give parameterizations of temperature dependence suitable for modeling purposes.

Experimental Section

The experimental setup will be only briefly introduced, because it has been described in detail elsewhere [8–13]. The experiments were carried out in a slow-flow reactor by using pulsed laser-photolytic production of OH radicals and pulsed laser-induced fluorescence detection of OH under pseudo-first order conditions in helium as bath gas. Intensity-time profiles of the fluorescence of OH were recorded by changing the delay time between the photolysis and probe laser pulses in steps of 0.2 μs .

The reactor was a T-shaped stainless steel cell with three quartz windows and an external resistance heating. The temperature was measured at the inlet and outlet of the cell with NiCr-Ni thermocouples. In each case, the temperature differences between these two thermocouples never exceeded 4 K. As reaction temperature the average of these temperatures was taken. In order to avoid accumulation of reaction products, the flow velocities were controlled with a mass flow controller. The chosen conditions assured that the complete content of the cell was exchanged between successive runs.

The precursor of OH radicals was nitric acid, which was photolyzed with a KrF-excimer laser at a wavelength of 248 nm. For OH detection, a XeCl-excimer laser operated at 308 nm was used to pump a dye laser (Coumarin 153) whose output was frequency-doubled with a BBO crystal. The non-resonant fluorescence of OH at $308 \pm 7.5 \text{ nm}$ was detected perpendicular to the photolysis and probe laser beam with a photomultiplier. In order to minimize scattered light, other wavelengths were filtered out with a monochromator. The time delay between photolysis and probe laser was set by a delay generator. For each given delay, ten measurements were recorded and automatically averaged. The repetition rate was 10 Hz.

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The gas mixtures were prepared in stainless steel gas cylinders and were allowed to homogenize for at least 12 h before use. There was no systematic dependence of the results on the cylinder filling level, which indicates that the gas mixtures were completely homogenized. Pressures were controlled by a series of pressure gauges. Nitric acid was freshly prepared from degassed concentrated sulfuric acid and dried sodium nitrate. The reaction mixture was slowly heated up to 333 K. In a direct vacuum distillation, nitric acid was collected in a separate flask cooled with liquid nitrogen. It was stored in the dark and degassed before use. The purities of the other substances were as follows: He > 99.999% (Air Liquide – Alphagaz), DMF \geq 99% (Sigma Aldrich), MF \geq 99% (Sigma Aldrich).

The experimental uncertainty is difficult to quantify exactly, because it is influenced by a multitude of factors as *e.g.* initial concentrations, temperature, pressure, and laser intensities. Therefore, a maximum error of 30 % for the rate coefficients was estimated.

Results and Discussion

The experiments on the DMF + OH reaction were carried out in the temperature range 295–561 K at pressures between 6.7 and 21 bar with initial concentrations of 1.22×10^{15} to 9.88×10^{15} cm $^{-3}$ for DMF and 7.84×10^{15} to 4.38×10^{16} cm $^{-3}$ for HNO $_3$. The MF + OH reaction was investigated in the temperature range 295–410 K at pressures between 12.8 and 21.1 bar. The initial concentrations ranged from 2.05×10^{15} to 9.86×10^{15} cm $^{-3}$ for MF and 9.47×10^{15} to 1.85×10^{16} cm $^{-3}$ for HNO $_3$. The initial OH concentration was estimated to be in the order of $\sim 10^{12}$ cm $^{-3}$.

In Fig. 1 an example of a measured LIF intensity-time profile is shown.

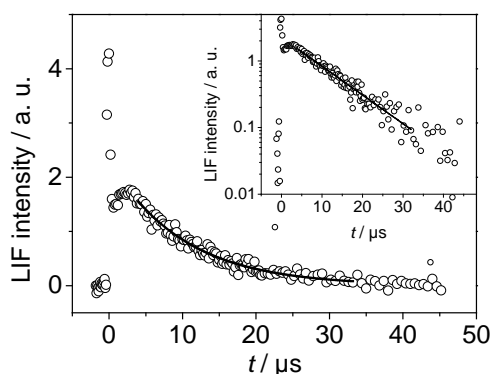


Fig 1. LIF intensity-time profile and exponential fit for MF + OH at $T = 370$ K, $P = 15.6$ bar and $[MF]_0 = 5.41 \times 10^{15}$ cm $^{-3}$.

The pseudo-first order rate coefficients, k_{pseudo} , can be obtained from the parameters of the exponential fit and the second-order rate coefficients, k_1 , followed from:

$$k_1 = \frac{k_{\text{pseudo}}}{[\text{furan}]_0} \quad (1)$$

To estimate the influence of side reactions, experiments with pure HNO $_3$ were performed, and the corresponding lifetimes of OH were determined. These lifetimes were around 0.1 ms, whereas the OH + furan reactions proceeded much faster on the μ s time scale. Obviously, any influence of side reactions can be neglected. To verify the pseudo-first order assumption, k_{pseudo} was plotted versus furan concentration. Figure 2 shows an example of such a plot. Note that the negative intercept is characteristic for this particular experimental run. In general intercepts scattered around zero, which can be explained by small errors in concentration due to mixture preparation.

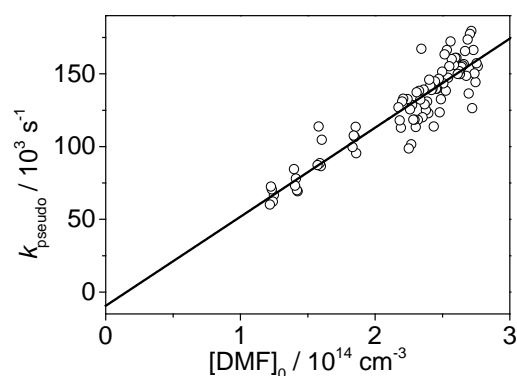


Fig. 2. Dependence of k_{pseudo} on the DMF concentration at $T = 295$ K and $6.7 \leq P/\text{bar} \leq 15.6$.

In general, 20 measurements were carried out for each temperature, and the resulting rate coefficients were averaged. An extended series of 85 measurements were performed over a pressure range from 6.7 to 15.6 bar at 295 K to examine the pressure dependence. The results for the DMF+OH reaction are shown in Fig. 3. The slope is around zero and therefore no pressure dependence is assumed. The same results were obtained for the MF+OH reaction.

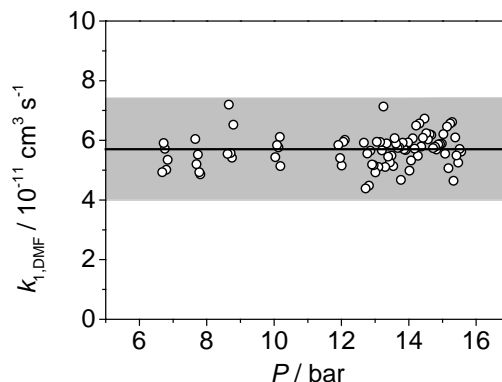


Fig. 3. Pressure dependence of the rate coefficient $k_{1,\text{DMF}}$ at $T = 295$ K with an estimated error of 30 % (gray area).

The temperature dependence of the rate coefficients is shown in Figs. 4 and 5, and a comparison with literature data is given. Bierbach *et al.* [5] and Aschmann *et al.* [6] measured rate coefficients at room temperature and atmospheric pressure.

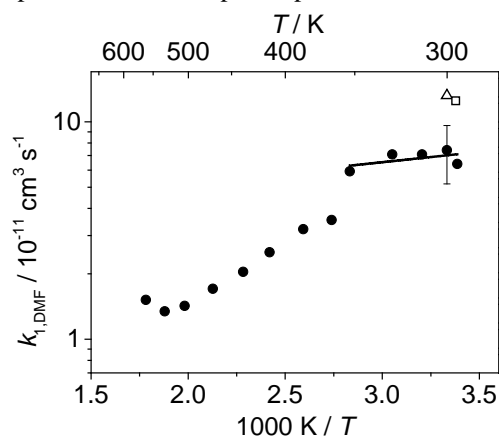


Fig. 4. Arrhenius plot of the measured rate coefficients $k_{1,DMF}$ (black circles) in comparison with the results from Bierbach *et al.* [5] (triangle) and Aschmann *et al.* [6] (square); (solid line) best fit according to eq. 2 for $295 < T/K < 350$; estimated error of $\pm 30\%$.

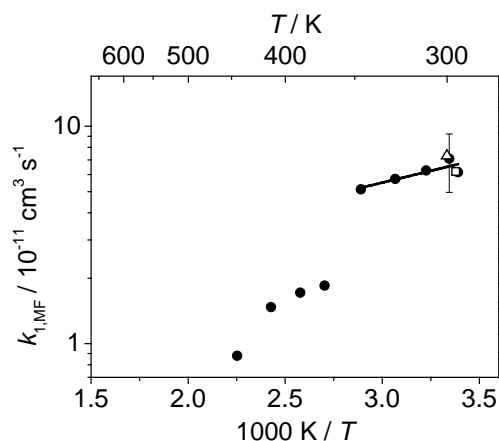


Fig. 5. Arrhenius plot of the measured rate coefficients $k_{1,MF}$ (black circle) in comparison with the results from Bierbach *et al.* [5] (triangle) and Aschmann *et al.* [6] (square); (solid line) best fit according to eq. 2 for $295 < T/K < 350$; estimated error of $\pm 30\%$.

If we compare our 298 K values of $k_{1,DMF}$ and $k_{1,MF}$ with these previous results, it is obvious that there is a disagreement of $\sim 55\%$ for DMF with the data from both Bierbach *et al.* [5] and Aschmann *et al.* [6]. For the OH + MF reaction, the value of $k_{1,MF}$ at 298 K agrees very well with all previous investigations.

The rate coefficients determined show a non-Arrhenius temperature dependence. In general, two different types of kinetic behavior were identified within specific temperature ranges. At $T < 350$ K the measured values of k_1 were nearly independent of temperature, whereas for $T > 350$ K a much more pronounced decrease was found.

Because of this particular behavior, an Arrhenius fit according to

$$\ln k_1 = \ln A - \left(\frac{E_a}{RT} \right) \quad (2)$$

is only useful in a limited range. Linear least-squares fits to the relevant points (see Figs. 4 and 5) result in the following expressions:

$$k_{1,DMF} = (3.38 \pm 1.00) \times 10^{-11} \exp\left(\frac{219 \text{ K}}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad (3)$$

$$T = 295\text{--}350 \text{ K}, P = 7\text{--}21 \text{ bar}$$

$$k_{1,MF} = (1.23 \pm 0.37) \times 10^{-11} \exp\left(\frac{500 \text{ K}}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad (4)$$

$$T = 295\text{--}350 \text{ K}, P = 13\text{--}21 \text{ bar}$$

The general temperature dependence is identical to those observed in reactions of OH with other unsaturated hydrocarbons, especially aromatic compounds. Figure 6 shows Arrhenius plots of our experimental results in comparison with other examples exhibiting the same behavior.

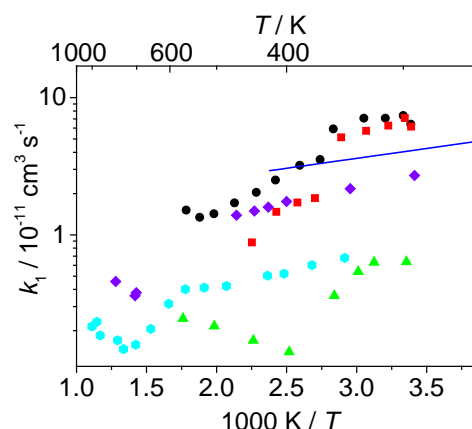


Fig. 6. Arrhenius plots of DMF + OH (black circles, this work), MF + OH (red squares, this work), furan + OH (blue line) [14], toluene + OH (green triangles) [15], ethane + OH (cyan hexagons) [16], propene + OH (purple diamond) [17].

Qualitatively, the forms are very similar, whereas the specific temperature ranges depend on the reactants. Based on the results of previous investigations and the present study, a consistent picture for the mechanism of OH reactions with unsaturated hydrocarbons begins to emerge. Often, three different regimes of temperature dependence can be identified. At low temperatures ($T \leq 320$ K) there are often slightly negative or positive temperature dependences. Here, the OH radicals predominantly add to the double bond or the aromatic ring system forming adducts that are thermally stable with respect to back dissociation. The intermediate temperature regime is characterized by increasing back

dissociation causing a more pronounced decrease of the rate coefficients with temperature. If temperature rises further, the OH adducts become thermally unstable with respect to forward dissociation, and the overall rate rapidly increases. In many previous investigations, non-exponential OH decays were observed in the intermediate regime [12, 15, 18, 19], whereas in our study only exponential OH decays occurred.

At temperatures above 500 K, the reactions proceed mainly *via* hydrogen abstraction, and, hence, the temperature dependence is positive here. In our OH + DMF experiments, this positive temperature dependence may be discernible at the highest temperature but cannot be safely assumed, of course, on the basis of one single value.

Among the reactions of OH with furan derivatives, the OH + furan reaction is obviously slower than the OH + MF and OH + DMF reactions. This may be explained by the stability of the OH adduct species. With increasing number of methyl groups, the radicals formed are increasingly stable.

Compared to the reaction of OH with toluene, the rate coefficients of the reactions of OH with furans are larger. In addition to the higher stability of the furan adduct radicals, back dissociation may be dominated by fast ring opening.

Summary and Conclusion

A detailed experimental study on the OH + DMF and the OH + MF reactions was performed. The experiments were carried out at 295–560 K for OH + DMF and 295–410 K for OH + MF in a pressure range of 7–21 bar. For neither of the two reactions, pressure dependence was observed. In the temperature range studied both reactions show non-Arrhenius temperature dependence with two kinetically different regimes. In the first regime ($T = 295\text{--}350\text{ K}$) the rate coefficients only slightly decrease with temperature, whereas above 350 K a much more pronounced decrease was found. Such a behavior can be explained by non-reversible addition of the OH radical to the aromatic ring in the first regime, and increasingly important thermal back-dissociation of the OH adduct in the second regime.

Furthermore, the experimentally determined rate coefficients at 298 K were compared with results published earlier by Bierbach *et al.* [5] and Aschmann *et al.* [6]. For the OH + DMF reaction, there is a disagreement of ~55 % whereas the value of $k_{1,\text{MF}}$ at 298 K agrees very good with all previous investigations.

Acknowledgement

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