Kinetics of the Reaction of OH Radical with the Biofuel Molecule 2-Methyltetrahydrofuran

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Abstract

2-methyltetrahydrofuran (2-MTHF) is a promising new biofuel and renewable platform molecule for the chemical industry. Its reaction with OH radical is of importance concerning both of its atmospheric fate and combustion. The low pressure discharge flow (DF) method coupled with OH-resonance fluorescence detection (RF) has been applied to determine k_1 (300 K, 2.6 mbar He) = (1.18 ± 0.16 (2σ)) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} rate coefficient for the overall reaction OH + 2-MTHF → products (1). The only other rate coefficient reported in the literature is about two times higher, but it was determined at higher pressures which may indicate possible pressure dependence. Relative-rate experiments (RR-GC) have also been performed, but provided inconclusive results.

Introduction

Biomass represents a huge renewable source of lignocellulosic feedstock for the production of chemicals, energy, and solvents providing the potential to replace fossil commodities and therefore to help mitigate global warming [1], [2], [3]. The cyclic ether 2-methyltetrahydrofuran, 2-MTHF is one of the most promising renewable biomolecules. It can be produced from biomass with high yields, for example, through levulinic (LA) acid by using homogeneous and heterogeneous catalytic processes. There has been a real boom in the organic chemistry literature concerning the catalytic conversion of biomass-derived feedstocks to valuable chemicals and biofuels [4] [5]-[8]. A schematic drawing of the different synthetic routes that are proposed for the "levulinic-acid family" has been depicted in Fig. 1. The title molecule 2-MTHF is often produced from LA through the intermediate γ-valerolactone (GVL) using a multitude of homogeneous and heterogeneous catalytic methods. Importantly, there have been more and more effective catalysts available that do not necessitate the use of expensive noble metals [4], [9], [10]. 2-MTHF is a versatile platform molecule, a 'green solvent' to replace tetrahydrofuran (THF), and it can be used favorably as a biofuel blended to gasoline [11].

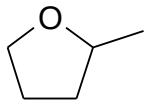
2-MTHF belongs to the group of second generation biofuels (2G) that are being produced from biomass, *i.e.*, non-edible cellulose, hemicellulose or lignin, and so it does not compete with food production, unlike the first generation biofuels (1G), such as corn ethanol [12]. Recently proposed LA-derived 2G biofuels, beside 2-MTHF, include ethyl levulinate (ELA) [4], the C5-cyclic ester, γ-valerolactone (GVL) [5], [13] and 2,5-dimethyltetrahydrofuran, (DMTHF) [14].

Moshammer and co-authors have recently published a very sophisticated experimental and detailed modeling study on the combustion and flame of 2-MTHF [15]. The authors have presented also a thorough overview of the related combustion literature [15].

Some release of 2-MTHF into the atmosphere is inevitable during its use as a biofuel in transportation or as a solvent in organic synthesis. Thus, we strongly believe that it is of vital importance to make reliable assessment of the atmospheric chemistry and environmental impact of this renewable chemical before its widespread use, as it should be in the case of any other industrial chemicals or alternative fuels proposed in recent years. In the atmosphere, the fate of 2-MTHF is essentially determined by the rate of its reactions with OH radicals. For an assessment of the atmospheric impact of 2-MTHF, rate coefficients for OH reactions at and below ambient conditions are needed. Moreover, rate parameters for the reactions of OH with 2-MTHF are needed in a wide range of temperature and pressure for the development of predictive chemical kinetic models for combustion applications.

Here we report rate coefficient for the reaction of OH radical with 2-MTHF at laboratory temperature (T = 300 K). Our work is part of a comprehensive experimental and theoretical study on the kinetics and photochemistry of 2G biofuels.

OH + 2-MTHF → products (1)



2-methyltetrahydrofuran, 2-MTHF.

2. Experimental

2.1 DF-RF Technique

The low pressure discharge flow apparatus (DF) and the OH resonance fluorescence detection system (RF)

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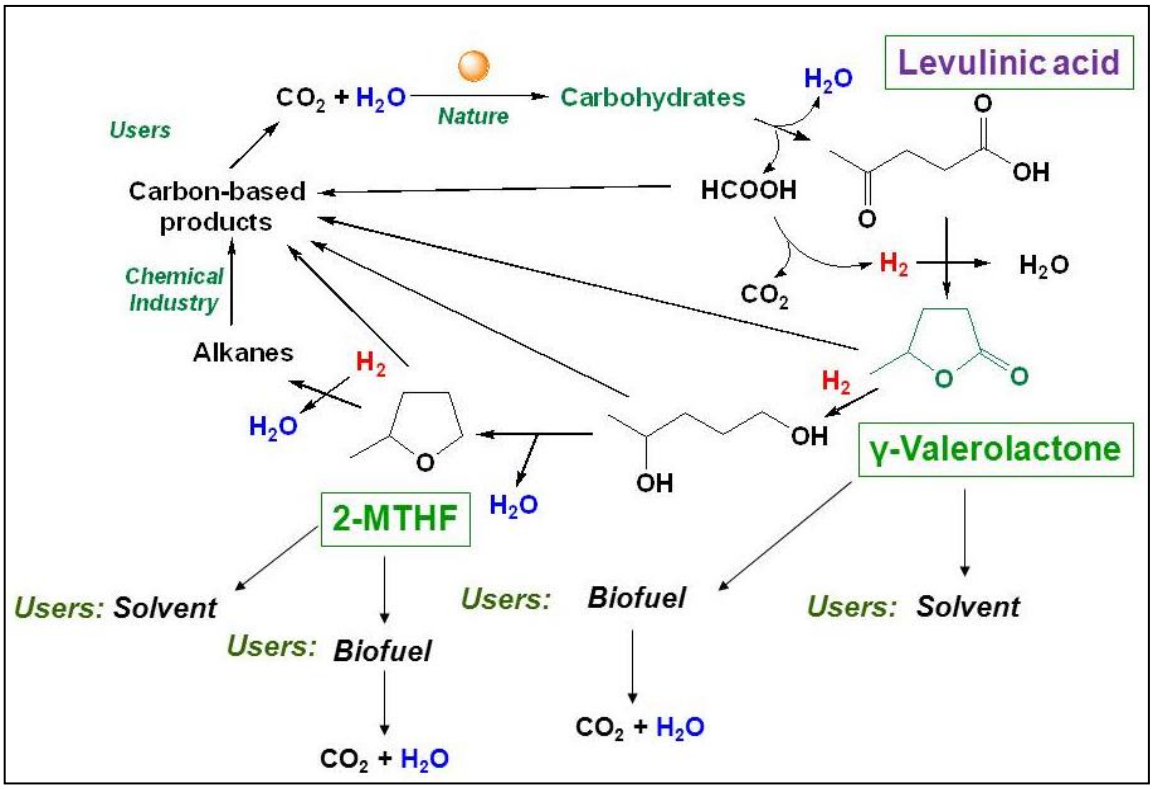

Fig.1. The levulinic acid biorefinery "family" based on the works by Horváth et al. [5] and Mehdi et al. [6].

have been described in detail previously in refs. [16] and [17, 18], respectively. A schematic drawing of the apparatus is presented in Fig. 2. Characteristic for our set-up is the vertically positioned flow-tube which is equipped with a moveable injector and operated by a versatile gas-handling and vacuum system. The flow-tube was constructed of Pyrex and had an inner diameter of 40.1 mm and an overall length of 600 mm. Its internal surface was coated with a thin layer of halocarbon wax (Halocarbon Corporation, Series 1200) to reduce the effect of heterogeneous wall reactions. The reaction pressure was measured using a calibrated capacitance manometer (MKS Baratron, 10 Torr head). The reactor was equipped coaxially with a moveable injector to vary the reaction time. The injector consisted of an outer tube of 16 mm o. d. surrounding a coaxial shorter tube of 6 mm o. d. OH was obtained by reacting H atoms with a slight excess of NO_2 inside the moveable injector: $H + NO_2 \rightarrow OH + NO$. Hydrogen atoms were generated by microwave-discharge dissociation of H_2, in large excess of He flow. Concentrations of the OH-source molecules were: $[NO_2] \approx 4 \times 10^{-12}$ and $[H_2] \approx 6 \times 10^{-12}$ molecule cm^{-3}. OH entered the flow-tube from the injector which had the advantage of providing constant initial OH concentration at each position of the injector. The DF technique allowed the reactions to be studied with ~0.5 ms time resolution. Helium was the carrier gas which was passed through liquid-nitrogen cooled activated silica gel traps for further purification.

The main gas flows were regulated and monitored by calibrated mass-flow controllers (Tylan, FC-260). Smaller flows were regulated by needle valves (Hoke, Micromite) and were determined by measuring the pressure rise in known volumes. The linear flow velocity was $v_{lin} \approx 2000$ cm s^{-1} corresponding to ~60 cm^3 s^{-1} volumetric flow rate. These flow rates are significantly faster than were in most of our previous experiments [16-18], but it was necessary to use because of the high rate of the studied reaction. Thus, the DF apparatus was operated by three high pumping capacity rotary pumps. The pumps were connected to the flow tube through large traps cooled with liquid nitrogen in order to avoid back diffusion of oil vapor and to remove corrosive vapors.

The lower end of the flow-tube was coupled to a black anodized aluminum fluorescence cell mounted with Suprasil windows. The OH radicals were detected by $A^2\Sigma^+$–$X^2\Pi$ (0,0) resonance fluorescence. The excitation radiation was produced by a microwave powered resonance lamp operated with flowing Ar/H_2O at ~2 mbar. The microwave energy was obtained from 2450 MHz microwave generators (Medical Supplies, Microtron 200 or AHF-Analysentechnik, GMW 24-303 DR). The induced RF radiation was collected at right angles to both the optical axis of the lamp and the gas stream and imaged onto the photocathode of a photomultiplier (EMI, 9781QB). The PM viewed the OH fluorescence through an interference filter with the

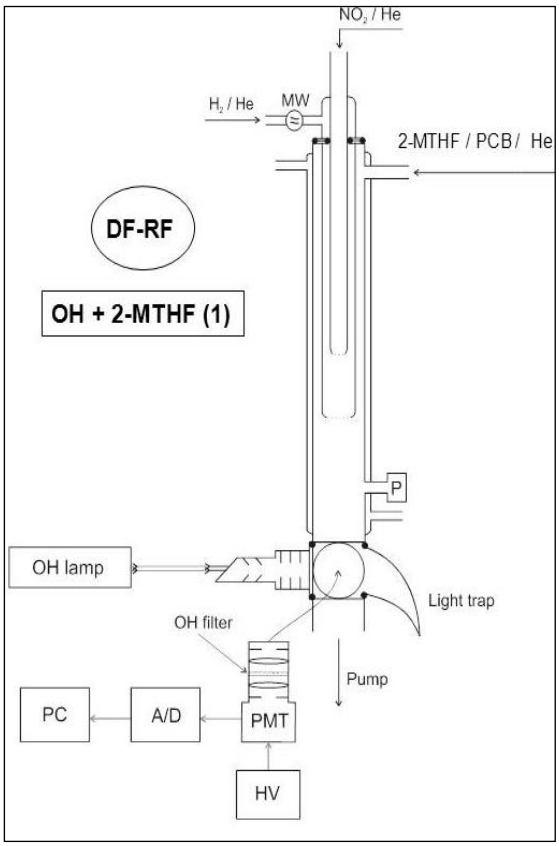

Fig.2. DF-RF apparatus and gas flows applied to study the kinetics of the OH + 2MTHF (1) reaction.

optical properties of λ_{max} = 307 nm, T_{max} = 25% and *FWHM* = 25 nm (LOT-Oriel).

The analogue signal from the PM was digitalized and transferred to a laboratory PC for averaging and further data acquisition using an integrated hardware-software system (H-Interorg Ltd). OH detection sensitivity was ~1×10^9 molecule cm^{-3}.

2.2 Relative-Rate Technique (RR-GC)

The relative-rate (RR) experiments were carried out in a 10 litre Pyrex photo-reactor (Fig. 3). For photolytic production of OH radicals, we have used a modified cinema projector, the light source of which was a 3 kW Xe lamp. A parabolic reflector collimated the light of the Xe lamp to a parallel beam of about 30 cm diameter. The irradiating light was passed through a heat reflecting mirror and three liquid [19]. The transmitted light had a maximum at 362 nm and a full width at half maximum of 28 nm. To maintain uniform irradiation conditions, the bulb was slowly rotated and a large Al-mirror was placed behind it.

OH radicals were produced by photo-oxidation of methyl nitrite in atmospheric pressure synthetic air:

$$CH_3ONO + h\,\nu \rightarrow CH_3O + NO$$
$$CH_3O + O_2 \rightarrow HO_2 + CH_2O$$
$$HO_2 + NO \rightarrow OH + NO_2$$

The reaction temperature was measured with a retractable thermocouple. The Pyrex reactor was equipped with a GC sampling port; samples for analysis were withdrawn by a gas-tight syringe through a septum connected to a glass capillary tube, which reached in the center of the bulb.

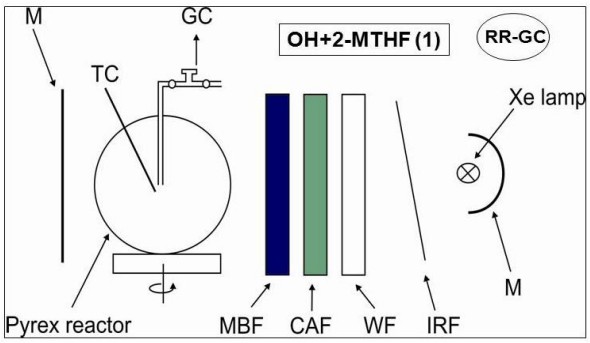

Fig.3. Experimental set-up for relative-rate kinetic measurements of reaction (1). M: mirror, IRF: infrared filter, WF: water filter, CAF: chrome alum filter, MBF: methylene blue filter, TC: retractable thermocouple.

The concentration depletion of the organic reactants was determined by temperature programmed gas chromatography (313–398 K) using a 30 m long 'FAME' quartz capillary column and flame-ionization detection.

Table 1
Materials used in the experiments

Name	Supplier	Purity (%)	Note
He	Messer-Griesheim	99.996	[a]
H_2	Messer Hungaria	99.95	[a]
Synthetic air	Messer Hungaria	≥99.99	[a]
NO_2	Messer-Griesheim	≥99	[b]
c-C_6H_{12}	Aldrich	> 99.5	[c,d]
2-MTHF	Aldrich	≥ 99	[e,b]
c-C_4F_8 (PCB)	PCR Inc.	99	[f, b]
CH_3ONO	Synthetsized	>99.5	[g,b]

[a] Used as provided; He was led through N_2(l) traps in the DF-RF experiments. [b] Purified by low temperature distillation in vacuum. [c] Degassed prior to use. [d] Reference reactant: *c*-hexane [e] 2-methyltetrahydofuran reactant (2-MTHF); the sample contained 250 ppm butyl-hydroxyl-toluol (BHT) as a stabilizer. [f] GC internal standard, perfluoro-cyclo-butane (PCB). [g] Prepared from methanol with nitrous acid [19-20] and was purified by multiple bulb-to-bulb distillations in vacuum and stored at 255 K in darkness.

2.3 Preparation of Gas Mixtures

Gas mixtures were used in the experiments, 2-MTHF/PCB/He for the DF-RF experiments and 2-

MTHF/c-C_6H_{12}/CH_3ONO/PCB/air for the RR-GC experiments that were prepared manometrically in 10 L Pyrex bulbs and were allowed to mix for at least 4 hours. The inert GC standard PCB served for determination of the concentrations of reactants in the gas mixtures: no measurable changes were observed during a few days of storage time. The liquid 2-MTHF samples contained 250 ppm butyl-hydroxyl-toluol (BHT) as a stabilizer. The boiling point of BHT (265 °C) is much higher than that of 2-MTHF (79 °C). Therefore, understood by the very different vapor pressures, no BHT was found in the gas mixtures by GC analysis.

3. Results and Discussion

3.1 DF-RF Determination of k_1(OH + 2-MTHF)

The experiments were conducted at T = 300 ± 3 K reaction temperature and P = 2.60 ± 0.10 mbar He pressure. (The uncertainties reported in this paper are two standard deviations and refer to precision only). The standard pseudo-first-order kinetic method was employed to determine rate constant for OH + 2-MTHF (1) employing a large excess of [2MTHF] over the initial hydroxyl radical concentration of $[OH]_0 \approx 1 \times 10^{11}$ molecule cm^{-3}. The 2-MTHF concentration was between 1.62 and 27.3 × 10^{12} molecule cm^{-3}. The experiments were performed by recording the OH resonance fluorescence signal magnitudes vs. the varied reaction distance, Δz, with, S_{on}, and without, S_{off}, of the reactant 2-MTHF flow. The experimental observables were evaluated by equations (I) – (III):

$$-\ln\left(\frac{S_{\text{on}}}{S_{\text{off}}}\right) = k_1' \times \frac{\Delta z}{\text{v}_{\text{lin}}} \qquad \text{(I)}$$

$$k_1' = k_1 \times [\text{2MTHF}] + const. \qquad \text{(II)}$$

$$-\ln S_{\text{off}} = k_{\text{w}} \times \frac{\Delta z}{\text{v}_{\text{lin}}} \qquad \text{(III)}$$

The measured hydroxyl decays, when plotted according to eqn. (I), displayed straight lines, the slopes provided the pseudo-first-order rate coefficient (decay constant), k_1'. Sample decay plots are presented in Fig. 4., and Fig. 5 shows a plot of k_1' versus [2-MTHF]; the bimolecular rate constant, k_1, was obtained by linear least-squares (LSQ) analysis. The plotted ln S_{off} vs. Δz data gave also straight lines, the slopes of which supplied the 'wall rate constant' of $k_w \approx 25$ s^{-1}. This is of the usual magnitude for heterogeneous loss of OH we observed previously for OH reactions with oxygenated organics. The experimental conditions and results are summarized in Table 2.

Table 2
DF-RF experimental conditions and kinetic results for the reaction OH + 2-MTHF (1) (T = 300 ± 3 K, p = 2.6 ± 0.1 mbar He)

[2-MTHF][a]	k'_1 [b]	v_{lin} [c]	k_w [d]	k_1 [e]	No.[f]
1.62–27.3	28–392	1930–2031	25±16	1.18±0.16	44

Units: [a]10^{12} molecule cm^{-3}, [b] s^{-1}, [c] cm s^{-1}, [d]s^{-1}, [e] 10^{-11} cm^3 molecule^{-1} s^{-1}. [f]Number of experiments

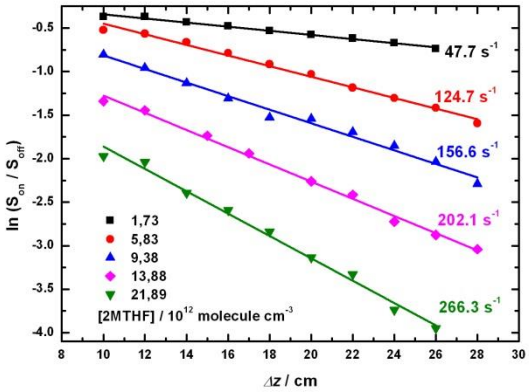

Fig.4. Typical semi-logarithmic OH decay plots from DF-RF experiments of reaction (1). Δz is the length of the reaction zone, S_{on} and S_{off} are the RF signal strengths with 2-MTHF flow 'on' and 'off', respectively.

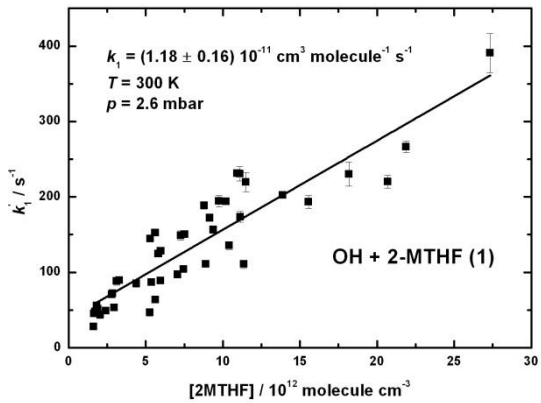

Fig.5. Plot of pseudo-first-order rate constant against the 2-methyltetrahydrofuran concentration. The slope provides k_1.

3.2 RR Determination of k_1(OH + 2-MTHF)

The RR experiments were carried-out at T = 301 ± 4 K reaction temperature, in p = 1060 mbar synthetic air. The rate constant ratio k_1/k_2 was estimated by comparing the rate of loss of 2-MTHF to that of the reference compound, c-hexane:

OH + 2-MTHF → products (1)
OH + c-C_6H_{12} → products (2)

The standard RR expression was used to evaluate the experimental data:

$$\ln\left(\frac{[2-\mathrm{MTHF}]_0}{[2-\mathrm{MTHF}]_t}\right) = \left(\frac{k_1}{k_2}\right) \times \left(\frac{[c-\mathrm{C_6H_{12}}]_0}{[c-\mathrm{C_6H_{12}}]_t}\right) \quad \text{(IV)}$$

where $[2\text{-MTHF}]_0$, $[2\text{-MTHF}]_t$, $[c\text{-}C_6H_{12}]_0$ and $[c\text{-}C_6H_{12}]_t$ are the concentrations at time t_0 and t, respectively and the rate coefficient of the reference reaction is known from the literature, k_2(298 K) = 7.49 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [20].

The measured relative rate data plotted according to Equation (IV) have displayed unexpectedly large scatter, probably because of heterogeneous reactions that occur on the irradiated surface of the bulb reactor. Thus, in the current stage of research we can propose only an upper limit by the RR-GC measurements: k_1 (298 K) < 3 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

3.3 Kinetics of the Reaction of OH with 2-MTHF

The recommended rate coefficient for the OH + 2-MTHF (1) reaction from our current work is the one that we have determined by low pressure DF-RF kinetic experiments, that is:

k_1 (300 K, 2.6 mbar He) = (1.18 ± 0.16 (2σ)) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}

To our knowledge, a single other kinetic study has been performed so far on the OH + 2-MTHF reaction [21]. Wallington and co-workers have applied both direct and relative-rate experiments by which they have proposed k_1 (298 K) = 2.2 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, that is, a value which is about two times higher than our determination. Since their experiments were carried out at higher pressures, above ~50 mbar, comparison with our data might indicate a possible pressure dependence of the reaction.

In a very recent theoretical paper, Simmie has reported the hydrogen abstraction reaction of OH with 2-MTHF to proceed through the formation of prereaction H-bonded complexes [22]. Should these complexes be stabilized by collisions, a pressure dependence of the overall reaction might occur.

2-MTHF reacts in a fast reaction with OH radical similarly to the longer chain-length aliphatic ethers [20]. It photo-dissociates only at very short wavelengths, it does not hydrolyze [10] and so its atmospheric depletion takes place predominantly *via* reaction with OH. With a typical tropospheric OH concentration of $[OH]_{global} \approx 1 \times 10^6$ molecule cm^{-3} and by utilizing the OH reaction rate constants from our current work, the atmospheric lifetime, $\tau \approx (k_1 \times [OH]_{global})^{-1}$, of ~1 day is estimated for 2-MTHF (T = 298 K). That is, a very short tropospheric lifetime is predicted. This estimation is based on the assumption of complete global mixing of 2-MTHF and so the actual, local lifetime is likely even significantly shorter.

Acknowledgements

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