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# Direct and relative rate coefficients for the gas-phase reaction of OH radicals with 2-methyltetrahydrofuran at room temperature

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**Abstract** 2-methyltetrahydrofuran (2-MTHF) is a renewable green solvent, a platform molecule for organic syntheses and a potential automotive fuel or fuel additive that can be produced efficiently from lignocellulosic biomass. Its reaction with OH radicals is important concerning both of its atmospheric fate and combustion. Kinetics of the overall reaction  $\text{OH} + 2\text{-MTHF} \rightarrow \text{products}$  (1) were studied at room temperature ( $T = 298 \pm 1$  K) using both direct and relative kinetic methods. The low pressure fast discharge flow (DF) experiments coupled with resonance fluorescence (RF) detection of OH have provided the direct rate coefficient of  $k_1(298 \text{ K}, 2.64 \text{ mbar He}) = (1.21 \pm 0.14 (\pm 2\sigma)) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The relative-rate experiments (RR) with gas-chromatographic (GC) analysis were performed at higher pressure in synthetic air using the reaction  $\text{OH} + \text{cyclohexane (}c\text{-C}_6\text{H}_{12}\text{)} \rightarrow \text{products}$  (2) as reference. The determined rate coefficient ratio  $k_1/k_2 = 3.80 \pm 0.17 (\pm 2\sigma)$  has been converted to  $k_1(298 \text{ K}, 1030 \text{ mbar air}) = (2.65 \pm 0.55 (\pm 2\sigma)) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This  $k_1$  value agrees reasonably well with the only other rate coefficient reported which was determined also at higher pressures. Comparison with the DF result indicates a possible pressure dependence of the reaction. Impact of 2-MTHF on the chemistry of the atmosphere has been briefly discussed.

**Keywords** Biomass-derived chemicals • 2-methyltetrahydrofuran • OH radicals • Reaction kinetics • Atmospheric chemistry

## Introduction

Biomass represents a huge renewable supply of lignocellulosic substances that can be used for the production of chemicals, energy, and solvents providing the potential to replace fossil commodities and therefore help mitigate global warming [1], [2], [3]. There has been a huge increase of the number of publications in the literature concerning the catalytic conversion of biomass and biomass-derived resources to “low carbon footprint” value-added chemicals including biofuels [4] [5]–[8]. The cyclic ether 2-methyltetrahydrofuran (2-MTHF) is one of the most promising renewable biomolecules. It can be produced from biomass through furfural, or levulinic acid (LA) with high yields. The title molecule 2-methyltetrahydrofuran is produced from LA through the C5-cyclic ester,  $\gamma$ -valerolactone (GVL), which in itself is also a versatile platform molecule, produced by using a multitude of homogeneous and heterogeneous catalytic methods. Importantly, there have been more and more efficient catalysts available that do not necessitate the use of expensive noble metals [4], [9].

2-MTHF is a particularly valuable alternative solvent for the pharmaceutical industry. It is an aprotic polar solvent to replace, e.g., tetrahydrofuran (THF), which is derived from fossil reserves and also dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), which is known harmful to the Earth’s protecting ozone layer. The physical and chemical properties of 2-MTHF, such as, its low solubility in water, higher boiling point and remarkable stability make attractive its application in syntheses involving organometallics and organocatalysis and also for processing lignocellulosic substances [10].

2-MTHF can also be used favourably as a biofuel blended to gasoline in a wide mixing range [11]. 2-MTHF belongs to the group of second generation biofuels (2G) that are 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], GVL [5], [13] and 2,5-dimethyltetrahydrofuran (DMTHF) [14]. Moshhammer and co-authors have recently published a sophisticated experimental and detailed modelling study on the combustion and flame of 2-MTHF [15]. The authors have presented also an in-depth overview of the related combustion literature [15]. In view of the excellent physical, chemical and fuel properties, environmental and potential economic advantages of 2-MTHF, its market-share is expected to grow rapidly in the future bringing down the price of this biomass-based chemical.

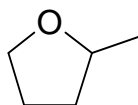
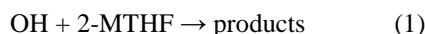
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Some release of 2-MTHF into the atmosphere is inevitable during its use as a biofuel in transportation or as a solvent in organic synthesis. Thus, we strongly believe that it is of vital importance to make reliable assessment of the atmospheric chemistry 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 radicals with 2-MTHF at room temperature ( $T = 298 \pm 1$  K) by using both absolute and relative kinetic methods. Our work is part of a series of experimental and theoretical investigations that have been in progress on the kinetics, photochemistry and catalysis of 2G renewables. Our preliminary results on the kinetics of the OH + 2-methyltetrahydrofuran (1) reaction have been reported in [16].



2-methyltetrahydrofuran, 2-MTHF.

## Experimental

### Discharge flow technique (DF–RF)

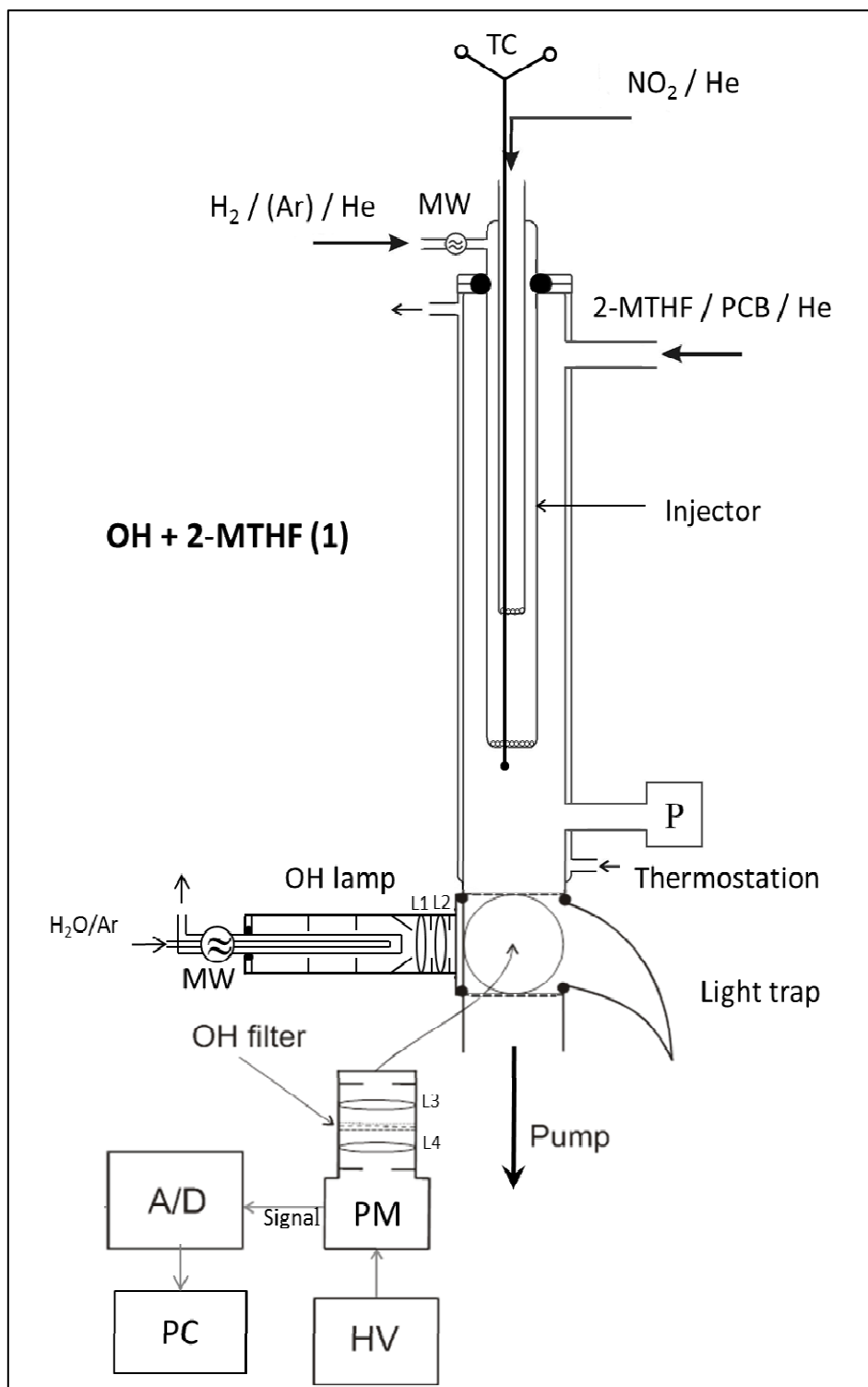
We have applied our conventional low pressure fast discharge flow apparatus (DF) coupled with resonance fluorescence (RF) detection of OH radicals [17–18] to perform the direct kinetic experiments. Since a few modifications of the apparatus have been made, we describe it here in some more detail; a schematic drawing of the apparatus is presented in Fig. 1.

As previously, our flow-tube reactor was positioned vertically providing a convenient way of its fitting with detection ports and gas introducing lines. The reactor 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 reactor was surrounded by a thermostating gown through which distilled water was circulated in the current experiments at room temperature by means of a thermostat (Julabo, F81-MV). The reaction pressure was measured at the downstream end of the reactor by 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 hydrogen atoms with a slight excess of NO<sub>2</sub> inside the moveable injector:  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ . H atoms were generated by 2450 MHz microwave dissociation of H<sub>2</sub> in a large excess of He flow (Medical Supplies, Microtron 200 generator) discharged in a quartz tube which was attached to the upstream end of the injector (Fig. 1). The gas stream passed through the discharge contained Ar in a small percentage (~0.002%) to facilitate dissociation of H<sub>2</sub>; the effective degree of dissociation was ~15%. OH entered the flow-tube from the injector through radially directed, ~1 mm diameter holes. This arrangement had the advantage of providing constant initial OH concentration at each position of the injector and facilitated fast mixing of the reactants. Concentrations of the OH-source molecules were:  $[\text{NO}_2] \approx 4 \times 10^{12}$  and  $[\text{H}_2] \approx 6 \times 10^{12}$  molecule cm<sup>-3</sup>.

The flow tube and the moveable injector were connected to a gas-handling vacuum system; flexible stainless-steel tubes (1 m × 12 mm i.d.) were used for the connection of the injector. The gas-handling system was operated by two-stage rotary vacuum pumps (Tungsramp BP-8 and Alcatel CIT) which also served for the evacuation of the flow-tube section between succeeding experiments; the goodness of the vacuum was monitored by Pirani gauges (Edwards, AGD 101M and MLW, PP-Vacuummeter). Gas mixtures, needed for the experiments were prepared on the vacuum line premixed with helium by using MKS Baratron pressure meters (10, 100 and 1000 Torr heads).

Helium was the carrier gas which entered the flow system through liquid-nitrogen-cooled activated silica gel traps for further purification. He flows were regulated and monitored by calibrated mass-flow controllers (Tylan, FC-260 and Aalborg, GFC 17). Smaller flows were regulated by needle valves (Hoke, Micromite) and were determined by measuring the pressure rise in known volumes by means of pressure transducers (EI Division and Schaewitz) connected to a strip-chart recorder (Radelkis, OH-814).

The average linear flow velocity was  $v_{\text{lin}} \approx 2000$  cm s<sup>-1</sup> corresponding to ~60 cm<sup>3</sup> s<sup>-1</sup> volumetric flow rate. This flow velocity is significantly faster than used previously in most of our DF experiments, e.g. in [17] and [19], but it was needed because of the high rate of the studied reaction. Thus, the apparatus was operated by three rotary



**Fig. 1** DF-RF apparatus and gas flows applied to study kinetics of the reaction of OH radicals with 2-methyltetrahydrofuran (2-MTHF). MW: microwave discharge; TC: thermocouple; PCB: GC internal standard, perfluoro-cyclo-butane (PCB); P: pressure meter; L1-L4: Suprasil lenses; PMT: photomultiplier; A/D: analogue-to-digital converter; PC: computer for signal averaging and data acquisition; HV: high voltage power supply.

pumps of high pumping capacities (Edwards 40-L, Edwards 80-L and Tungsram BPL-25). The pumps were connected to the flow tube through large traps cooled with liquid nitrogen in order to avoid back diffusion of oil vapour and for removing condensable corrosive vapours. The DF technique allowed the reaction to be studied with  $\sim 0.3$  ms time resolution.

The lower end of the flow tube was coupled to a black-anodised aluminum fluorescence cell mounted with Suprasil (Heraeus) windows. The OH radicals were detected by  $A^2\Sigma^+ - X^2\Pi(0,0)$  resonance fluorescence (RF), and a microwave-powered discharge lamp provided the exciting RF radiation (AHF-Analysentechnik, GMW 24-303 DR generator). A novel construction RF lamp assembly was used in the experiments (Fig. 1). The lamp was a coaxially arranged double quartz tube through which water-saturated Ar ( $\sim 1\%$   $H_2O$  in Ar) was flown at  $\sim 1$  mbar pressure. The optimal flow and pressure conditions for the RF lamp were set by a needle valve (Hoke, Micromite) and a pressure meter (MKS Baratron, 10 Torr head).

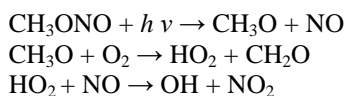
The induced RF radiation was collected at right angles to both the optical axis of the lamp and the gas stream and imaged onto the photocathode of a photomultiplier (EMI, 9781QB). The PM viewed the OH fluorescence through an interference filter with the optical properties of  $\lambda_{\max} = 307$  nm,  $T_{\max} = 25\%$  and  $FWHM = 25$  nm (LOT-Oriel). Blackened baffles and light traps were used to reduce scattered light in the detection volume.

The analogue signal from the PM was digitalized and transferred to a laboratory PC for averaging and further data acquisition using a purpose-built hardware-software system (H-Interorg Ltd, 2013) which provided an on-line estimation of the rate coefficient of the reaction. OH detection sensitivity was  $\sim 1 \times 10^9$  molecules  $cm^{-3}$ .

The 2-methyltetrahydrofuran (2-MTHF) reactant was introduced into the reactor from 2-MTHF/PCB/He gas mixtures that were prepared manometrically in 10 L Pyrex bulbs and were allowed to mix for at least 4 hours prior to use; the 2-MTHF concentration was typically  $\sim 5\%$ . The inert internal GC standard perfluoro-cyclo-butane (PCB) served for determination of the accurate concentration of 2-MTHF 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. No BHT has been found in the gas mixtures by GC analysis in line with that the boiling point of BHT (265 °C) is much higher than that of 2-MTHF (79 °C).

#### Relative-rate technique (RR-GC)

The relative-rate (RR) kinetic experiments were carried out in a 19.8 cm (optical length)  $\times$  2.1 cm (internal diameter) jacketed cylindrical quartz cell which was fitted with Suprasil windows and was thermostated to room temperature by means of a thermostat (Julabo, F81-MV). The photolysis cell was equipped with a GC sampling port, which included a septum joint and could be evacuated separately. The reaction temperature inside the cell was measured with a retractable thermocouple and was found constant at 1 K. OH radicals were produced by photo-oxidation of methyl nitrite in atmospheric pressure synthetic air:



For photolytic production of OH radicals, we used a modified cinema projector, the light source of which was a 3 kW Xe lamp. This light source is of much higher power than required for the current kinetic experiments, but it is intended to be used also for a subsequent product study of the OH/2-MTHF/air photo-oxidation reaction system using a large-volume photoreactor. A parabolic reflector collimated the light of the Xe lamp to a parallel beam and was passed through a heat reflecting mirror and three water filters of 11 cm optical paths each to remove the heat ballast. The middle part of the light beam entering the photolysis cell was cut by a 20 cm diameter blend bored in the middle of a blackened metal plate and the light intensity was reduced by metal sieves.

The reaction mixtures contained  $(1.48-2.72) \times 10^{16}$  molecules  $cm^{-3}$  2-MTHF reactant,  $(0.70-1.16) \times 10^{16}$  molecules  $cm^{-3}$  *c*-C<sub>6</sub>H<sub>12</sub> reference reactant,  $0.4 \times 10^{16}$  molecules  $cm^{-3}$  *c*-C<sub>4</sub>F<sub>8</sub> (internal GC standard),  $\sim 5 \times 10^{16}$  molecules  $cm^{-3}$  methyl nitrite, and synthetic air close to 1 bar. The gas mixtures were prepared on a conventional vacuum line in a 10 L Pyrex bulb using MKS Baratron pressure gauges (10 and 1000 Torr heads). In a test experiment, the reaction mixture was allowed to stand for 48 hours in the dark in the 10 L Pyrex container: there was no observable loss of the reactants.

The concentration depletions of 2-MTHF and the *c*-C<sub>6</sub>H<sub>12</sub> reference compound were determined by temperature programmed gas-chromatography (GC) between 100 and 160 °C using flame ionization (FID) detection (Agilent, 7890A GC). A QS-BOND (Restek) fused silica capillary column (30 m  $\times$  0.53 mm  $\times$  20  $\mu$ m film thickness) served for the separation of the compounds; He was the carrier gas. During analysis, the sampling line of the reactor was flushed through with the reaction mixture and samples for GC analysis were withdrawn by a gastight syringe.

The quoted uncertainties are two standard deviations throughout the paper and represent precision only. The errors are typically those that have returned from standard curve fitting procedures and have always been propagated for the derived quantities. Suppliers and purities of the materials used in the DF-RF and RR-GC experiments have been summarized in Table 1.

**Table 1** Materials used in the experiments

| Name  | Supplier         | Purity (%)         | Note |
|---|------------------|--------------------|------|
| He  | Messer-Griesheim | 99.996             | a    |
| H <sub>2</sub>                                | Messer Hungaria  | 99.999             | a    |
| Synthetic air                                 | Messer Hungaria  | ≥ 99.99            | a    |
| Ar  | Linde            | 99.995             | a,b  |
| H <sub>2</sub> O                              |                  | Ion exchange water | b    |
| NO <sub>2</sub>                               | Messer-Griesheim | ≥ 99               | c    |
| 2-MTHF  | Aldrich          | ≥ 99               | d, e |
| <i>c</i> -C <sub>4</sub> F <sub>8</sub> (PCB) | PCR Inc.         | 99                 | e, f |
| <i>c</i> -C <sub>6</sub> H <sub>12</sub>      | Aldrich          | ≥ 99               | e, g |
| CH <sub>3</sub> ONO                           | Synthesized      | >99.5              | h, c |

<sup>a</sup> Used as provided; He was passed through N<sub>2</sub>(l) traps filled with activated silica gel before entering the flow reactor

<sup>b</sup> Used for the operation of the OH resonance fluorescence lamp

<sup>c</sup> Purified by multiple low temperature distillations in vacuum until the frozen NO<sub>2</sub> became ‘bright white’

<sup>d</sup> 2-methyltetrahydrofuran (2-MTHF); the liquid sample contained 250 ppm butyl-hydroxyl-toluol (BHT) as a stabilizer

<sup>e</sup> Degassed prior to use

<sup>f</sup> GC internal standard, perfluoro-cyclo-butane (PCB)

<sup>g</sup> Reference reactant, cyclohexane (*c*-C<sub>6</sub>H<sub>12</sub>)

<sup>h</sup> Prepared from methanol with nitrous acid [20] and purified by multiple bulb-to-bulb distillations in vacuum and stored at 255 K in darkness

## Results

### Determination of $k_1$ from DF–RF experiments

The discharge flow experiments were conducted at  $T = 298 \pm 1$  K reaction temperature and  $p = 2.64 \pm 0.10$  mbar He pressure. The standard pseudo-first-order kinetic method with the plug-flow approximation was employed to determine rate coefficient for the overall reaction of OH with 2-MTHF using a large excess of [2-MTHF] over the initial hydroxyl radical concentration of  $[\text{OH}]_0 \approx 1 \times 10^{11}$  molecule  $\text{cm}^{-3}$ . The 2-MTHF concentration was varied between  $1.65$  and  $27.3 \times 10^{12}$  molecules  $\text{cm}^{-3}$ . The experiments were performed by recording the OH resonance fluorescence signal magnitudes vs. the varied reaction distance,  $\Delta z$ , with,  $S_{\text{on}}$ , and without,  $S_{\text{off}}$ , of the reactant 2-MTHF flow. The experimental observables were evaluated by equations (I) – (III):

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

$$k_1' = k_1 \times [2 - \text{MTHF}] + \text{const} \cdot \quad (\text{II})$$

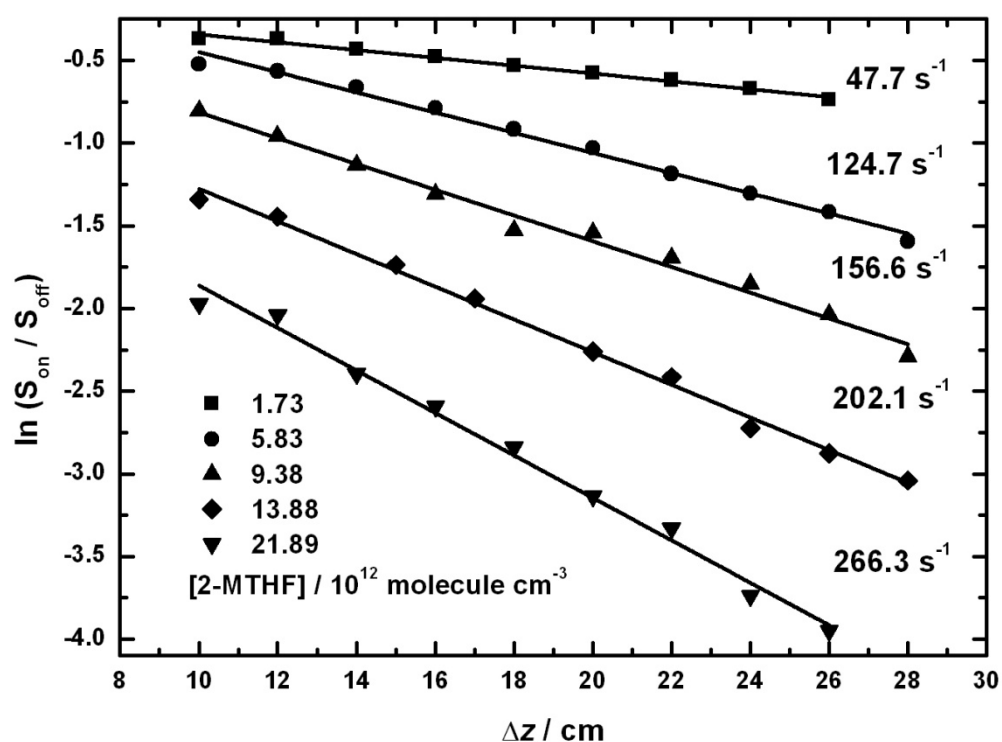
$$-\ln S_{\text{off}} = k_w \times \frac{\Delta z}{v_{\text{lin}}} \quad (\text{III})$$

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. 2, and Fig. 3 shows a plot of  $k_1'$  versus [2-MTHF]; the bimolecular rate coefficient,  $k_1$ , was obtained by weighted linear least-squares (LSQ) analysis. The plotted  $\ln S_{\text{off}}$  vs.  $\Delta z$  data gave also straight lines, the slopes of which supplied the ‘wall rate coefficient’ of  $k_w \approx 25 \text{ s}^{-1}$ . This is of the usual magnitude for heterogeneous loss of OH we observed previously for OH reactions with oxygenated organics. No corrections of the pseudo-first-order rate coefficients have been made for axial and radial diffusional effects and viscous pressure drop. Estimations by reported formulas [21–22] have shown the corrections to be small and partially cancelling each other’s effect for our experimental conditions. The experimental parameters and kinetic results have been summarized in Table 2.

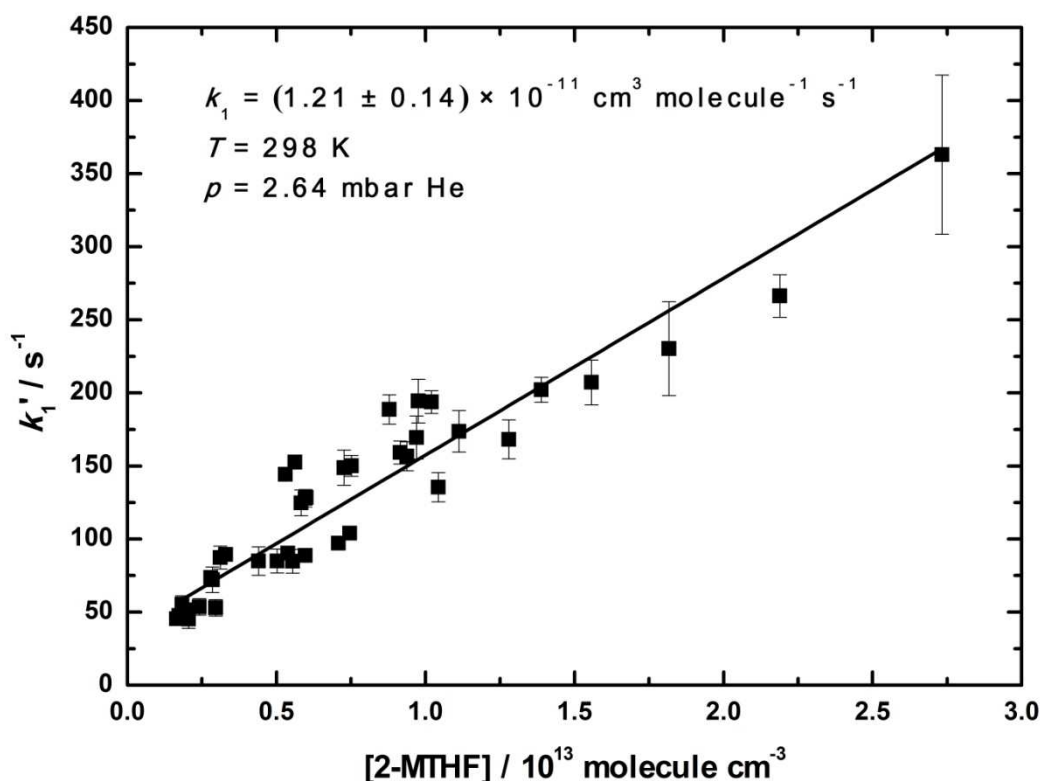
**Table 2** Experimental conditions and kinetic results for the DF-RF study of the OH + 2-MTHF (1) reaction ( $T = 298 \pm 1$  K,  $p = 2.64 \pm 0.10$  mbar He)

| $10^{-13} \times [2\text{-MTHF}]$<br>(molecules $\text{cm}^{-3}$ ) | $k_1'$ ( $\text{s}^{-1}$ ) | $v_{\text{lin}}$ ( $\text{cm s}^{-1}$ ) | $k_w$ ( $\text{s}^{-1}$ ) | $10^{11} \times k_1$<br>( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) | No. <sup>a</sup> |
|--|----------------------------|---|---------------------------|--|------------------|
| 1.65–27.3  | 45–363                     | 1100–2100                               | $25 \pm 8$                | $1.21 \pm 0.14$  | 39               |

<sup>a</sup> Number of  $k_1'$  determinations



**Fig. 2** Typical semi-logarithmic OH decay plots from DF-RF experiments of reaction (1). The numbers attached to the straight lines are pseudo-first-order rate coefficients measured at the respective 2-MTHF concentrations.



**Fig. 3** Plot of pseudo-first-order rate coefficients against the 2-methyltetrahydrofuran concentration. The slope provides  $k_1$ .

#### Determination of $k_1$ from RR–GC experiments

The relative-rate experiments were carried out at  $T = (298 \pm 1)$  K reaction temperature in  $p = (1030 \pm 20)$  mbar synthetic air. The rate coefficient ratio,  $k_1/k_2$ , was obtained by comparing the rate of loss of the reactant 2-methyltetrahydrofuran (2-MTHF) to that of the reference compound, *c*-hexane (*c*-C<sub>6</sub>H<sub>12</sub>).



Provided that the reactant and the reference compound are removed solely by reactions with OH radicals and are not reformed in any process, the standard RR expression is derived:

$$\ln\left(\frac{[2\text{-MTHF}]_0}{[2\text{-MTHF}]_t}\right) = \left(\frac{k_1}{k_2}\right) \times \ln\left(\frac{[c\text{-C}_6\text{H}_{12}]_0}{[c\text{-C}_6\text{H}_{12}]_t}\right) \quad (\text{IV})$$

where  $[2\text{-MTHF}]_0$ ,  $[2\text{-MTHF}]_t$ ,  $[c\text{-C}_6\text{H}_{12}]_0$ , and  $[c\text{-C}_6\text{H}_{12}]_t$  are the concentrations at time  $t = 0$  and subsequent times,  $t$ . Thus, a plot of  $\ln([2\text{-MTHF}]_0/[2\text{-MTHF}]_t)$  against  $\ln([c\text{-C}_6\text{H}_{12}]_0/[c\text{-C}_6\text{H}_{12}]_t)$  should be a straight line with slope of  $k_1/k_2$  and intercept of zero. The data obtained from several irradiations are plotted according to equation (IV) in Fig. 4. Linear least-squares (LSQ) fitting procedure yields the rate coefficient ratio  $k_1/k_2 = (3.80 \pm 0.17)$  and an intercept of zero within the experimental uncertainties.

The determined rate coefficient ratio has been put to an absolute scale by making use of the rate coefficient of the reference reaction  $\text{OH} + c\text{-C}_6\text{H}_{12}$  (2) recommended by Atkinson in his critical data evaluation,  $k_2$  (298 K) =  $(6.97 \pm 1.41) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [23]. In this way, the rate coefficient of  $k_1$  (298 K, 1030 mbar air) =  $(2.65 \pm 0.55) \times 10^{-11}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> is obtained. Results of the RR–GC experiments have been summarised in Table 3.

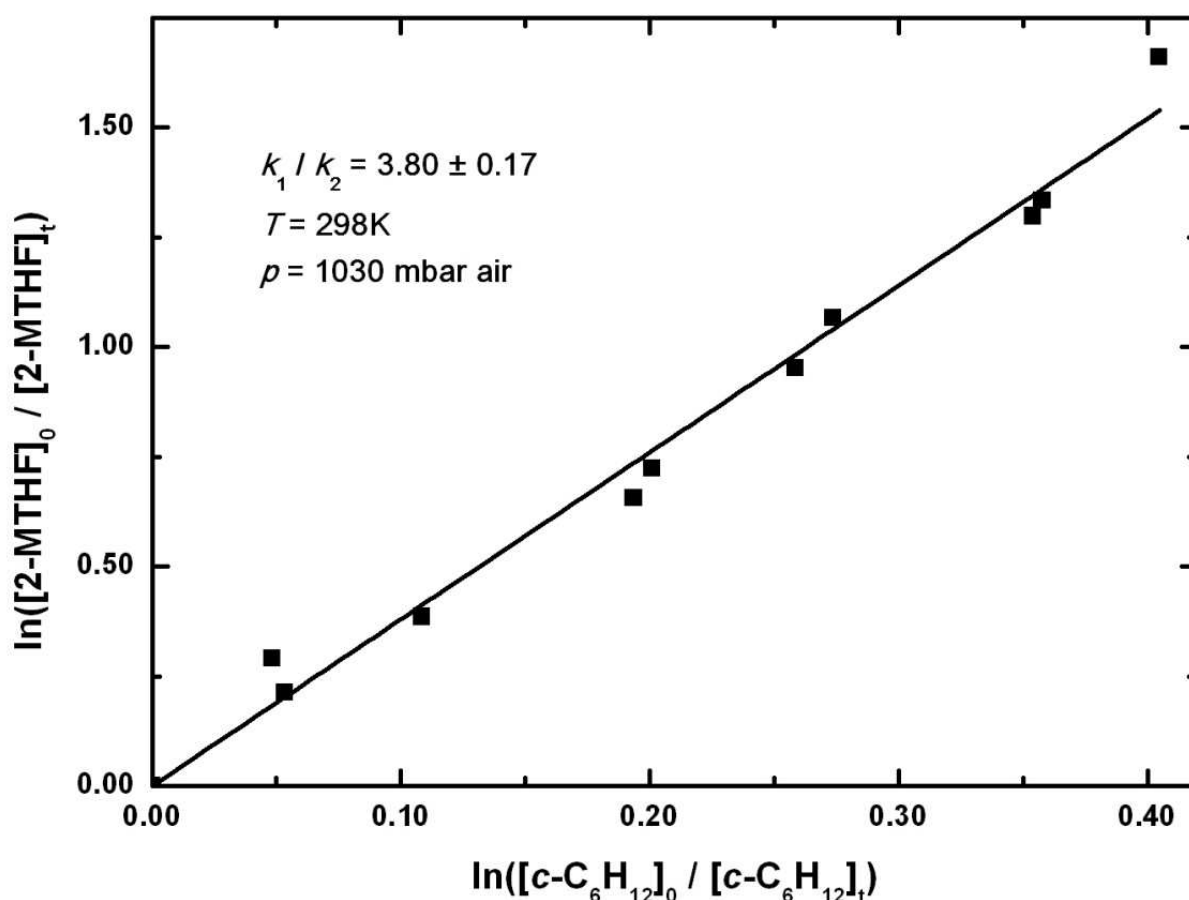


**Table 3** Experimental conditions and kinetic results for the reaction of OH radicals with 2-MTHF using the relative-rate kinetic method with *c*-C<sub>6</sub>H<sub>12</sub> as the reference reactant ( $T = 298 \pm 1$  K,  $p = 1030 \pm 20$  mbar synthetic air)

| $10^{-16} \times [2\text{-MTHF}]_0$<br>(molecules cm <sup>-3</sup> ) | $10^{-16} \times [c\text{-C}_6\text{H}_{12}]_0$<br>(molecules cm <sup>-3</sup> ) | $k_1/k_2$         | $10^{12} \times k_2$<br>(cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) | $10^{11} \times k_1$<br>(cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) | No. <sup>a</sup> |
|--|--|-------------------|---|---|------------------|
| 1.48–2.72  | 0.70–1.16  | $(3.80 \pm 0.17)$ | $6.97 \pm 1.41$ <sup>b</sup>  | $2.65 \pm 0.55$   | 11               |

<sup>a</sup> Number of RR data points (see Fig. 4)

<sup>b</sup> Taken from [23]



**Fig. 4** Relative-rate plot used to determine the rate coefficient ratio  $k_1(\text{OH} + 2\text{-MTHF})/k_2(\text{OH} + c\text{-C}_6\text{H}_{12})$

## Discussion

Kinetics of the reaction of OH with 2-MTHF

The following rate coefficients are obtained for the reaction  $\text{OH} + 2\text{-MTHF}$  (1) from our current work:

DF–RF result:

$$k_1(298 \text{ K}, 2.64 \text{ mbar He}) = (1.21 \pm 0.14 (\pm 2\sigma)) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

RR–GC result:

$$k_1(298 \text{ K}, 1030 \text{ mbar air}) = (2.65 \pm 0.55 (\pm 2\sigma)) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The determined rate coefficients are large values displaying high reactivity of OH with the cyclic ether 2-MTHF similarly to open-chain aliphatic ethers, see, e.g., [24–26] and references therein. It is to be noted, moreover

that the  $k_1$  value determined at  $\sim 3$  mbar is less than half of that measured at  $\sim 1$  bar suggesting a possible pressure dependence of the reaction.

To our knowledge, a single other kinetic study has been reported on the reaction of OH radicals with 2-methyltetrahydrofuran [27]. Wallington and co-workers applied the direct technique of flash photolysis (FP) coupled with RF monitoring of OH and also the relative-rate technique of stationary photolysis (SP) combined with FTIR analysis by performing the experiments in 47 mbar Ar and 980 mbar synthetic air, respectively [27]. They have concluded the results obtained with the two methods to agree well and proposed a room temperature rate coefficient of  $k_1(298\text{ K}) = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our RR–GC rate coefficient is higher by  $\sim 19\%$  and the low pressure DF–RF rate coefficient is lower by a factor of  $\sim 1.8$ . If one compares the high pressure RR results only, our rate coefficient agrees within error limits with that reported by Wallington et al.:  $k_1(295\text{ K}, 980\text{ mbar air}) = (2.53 \pm 0.31)$  [27] and  $k_1(298\text{ K}, 1030\text{ mbar air}) = (2.65 \pm 0.55)$ , this work, both given in  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Reaction (1) is anticipated to proceed via H-atom abstraction. There are several examples in the recent chemical kinetic literature revealing that many of the hydrogen abstraction reactions of OH radicals proceed via the formation of hydrogen-bonded ‘pre-reaction’ complexes (PRCs) which frequently give rise to specific kinetic features, such as a pressure dependence and unusual temperature dependence (see, e.g., the review papers of [28–29] and [30]). In a very recent theoretical article, Simmie has reported on the kinetics, mechanism and thermochemistry of the reactions of cyclic ethers with different free radicals including the reaction of OH with 2-MTHF [31]. Simmie has performed high level quantum chemistry computations and found the abstraction by OH to occur through the formation of PRC along the reaction path possessing the sizable binding energy of  $\sim(-23)$   $\text{kJ mol}^{-1}$ . The computations have shown abstraction from methyl to be negligible compared with abstraction of ring H-atoms which occur through negative barriers [31] in accordance with the high rate coefficient measured experimentally.

Experimental observation of a pressure dependence may indicate that the reaction system behaves chemically activated: the pre-reaction complex is formed vibrationally-rotationally excited, which, beside transforming to products, may undergo the competitive processes of reformation back to reactants and deactivation by collisions with the bath gas molecules giving rise to a decrease of the overall reaction rate coefficient with decreasing pressure. While this explanation is believed to be a reasonable one, it is also clear that the pressure dependence should be more firmly established by performing further kinetic experiments in a wide pressure range, and preferably, supplemented by statistical rate theory computations.

#### Implications for atmospheric chemistry

2-MTHF reacts in a fast reaction with OH radicals, it photo-dissociates only at very short wavelengths, does not hydrolyse [32] and so its atmospheric depletion takes place predominantly *via* reaction with OH. We have used the OH reaction rate coefficient of  $k_1 = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  we have determined at 1 bar and room temperature to estimate the tropospheric lifetime of 2-MTHF with respect to its reaction with OH radicals,  $\tau_{\text{OH}}$ . With an average global OH concentration of  $[\text{OH}]_{\text{global}} = 1 \times 10^6 \text{ radicals cm}^{-3}$  (24 h average) [33–34], the tropospheric lifetime of  $\tau_{\text{OH}} \approx 1/(k_1(298\text{ K}) \times [\text{OH}]_{\text{global}}) = 11$  hours is estimated. That is, a very short tropospheric lifetime is predicted. It is noted that this estimation is based on the assumption of complete global mixing of 2-MTHF which is clearly not the case in view of the short lifetime and the average tropospheric transport time-scale of a few months.

The short lifetime implies that 2-MTHF will be degraded close to its emission sources affecting air quality at

local and regional scales, most prominently through formation of ozone. Ground-level ozone is a priority air pollutant that is toxic, a potent greenhouse gas that has direct and indirect effects on the Earth's climate system [34]. Different atmospheric organics (VOCs) have different ability to contribute to ozone formation, which can be quantified by using the ranking parameter of POCP (Photochemical Ozone Creation Potential) developed by Derwent and co-workers – see, e.g. [35] and [36]. POCP values are derived by atmospheric chemistry models [35–36], via calculation of the total additional ozone at adding a given amount of VOC relative to the addition of the same amount of ethene (the POCP for ethene is defined as 100). Jenkin has proposed a simplified method to estimate POCP values for organic molecules,  $\epsilon^{\text{POCP}}(\text{VOC})$  [37]. The estimation procedure uses the fundamental molecular properties of the VOCs (molecular mass, number of carbon atoms, number of C–C and O–H bonds), rate coefficients for OH reactions (including OH + ethene) at 298 K and in 1 bar air, as well as empirical parameters depending on the types of organic molecules [37] – see also a summary of the method in [24].

Using Jenkin's method and our rate coefficient measured at ambient conditions, we have estimated a value of  $\sim 35$  for  $\epsilon^{\text{POCP}}(2\text{-MTHF})$ . This is less than the POCPs of reactive hydrocarbons or >C4 ethers and alcohols [24], [35–36] indicating that the practical use of the renewable biomolecule 2-methyltetrahydrofuran will likely not lead to a deterioration of air quality. A more sound assessment of the atmospheric impact would be expected from experimental and modelling studies of the atmospheric photo-oxidation of 2-MTHF.

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