



## Rate constant of the reaction between CH<sub>3</sub>O<sub>2</sub> and OH radicals



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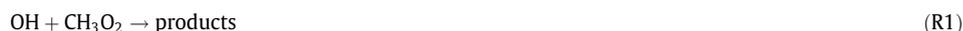
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### ABSTRACT

The rate constant of the reaction



has been measured at 294 K by simultaneous coupling of Laser Induced Fluorescence (LIF) and cw-Cavity Ring Down Spectroscopy (cw-CRDS) to laser photolysis. OH radicals were generated by 248 nm photolysis of either H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> in the presence of H<sub>2</sub>O, CH<sub>3</sub>O<sub>2</sub> radicals were generated simultaneously by photolysis of CH<sub>3</sub>I and their absolute concentrations were obtained by cw-CRDS. OH decays were measured under excess CH<sub>3</sub>O<sub>2</sub> concentrations and a very fast rate constant of  $k_1 = (2.8 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  was found independent of pressure at 50 and 100 Torr helium.

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### 1. Introduction

Peroxy alkyl radicals (RO<sub>2</sub>) are key reaction intermediates in the low temperature oxidation of organic compounds and play a central role in atmospheric chemistry [1]. They are predominantly formed from the initial reaction of OH radicals with hydrocarbons, leading to formation of an alkyl radical R:



followed by recombination of the alkyl radical with molecular oxygen



In polluted environments, peroxy radicals react predominantly with NO, leading to formation of NO<sub>2</sub>, which through subsequent photolysis leads to formation of O<sub>3</sub>.

At low NO<sub>x</sub> concentrations such as in the remote continental boundary layer, the marine boundary layer, and the background troposphere, the lifetimes of RO<sub>2</sub> radicals increase and other reaction pathways become competitive for peroxy radicals. Atmospheric chemistry models consider the major fate for RO<sub>2</sub> radicals under these conditions through self- and cross reactions with other RO<sub>2</sub> radicals or with HO<sub>2</sub> radicals [2], in the example of CH<sub>3</sub>O<sub>2</sub>:



Currently, the reaction of RO<sub>2</sub> radicals with OH radicals is not considered in models, even though if fast enough to compensate for the roughly 2 orders of magnitude lower OH concentration compared to HO<sub>2</sub> or RO<sub>2</sub>, it might become competitive with (R4) and (R5). In a recent modeling study, Archibald and co-workers [3] have investigated the impact of including the reaction between RO<sub>2</sub> and OH on the composition of the Marine Boundary Layer (MBL). They have run different scenarios using a model named BAMBO, based on the MCM mechanism [2]. Different possible reaction paths and rate constants were simulated for peroxy radicals up to C<sub>4</sub>, leading for the simplest one, CH<sub>3</sub>O<sub>2</sub>, to the following products:



For all scenarios they found only a small, negligible effect on the mixing ratios of O<sub>3</sub>, NO<sub>x</sub>, OH and other trace gas species in the marine boundary layer. However, a substantial increase in the mixing ratios of HCOOH was observed (from 0.16 ppt in the base case, i.e. absence of (R1), to 25.5 ppt at the highest rate constant scenario, if the reaction pathway would be formation of the Criegee radical (R1a). A strong increase in the mixing ratio of CH<sub>3</sub>OH (from 37 ppt in the base case, i.e. absence of (R1), to 294 ppt at the highest rate constant scenario), was observed if the major pathway would be (R1c). The impact on the RO<sub>2</sub> and HO<sub>2</sub> radical budget was below 10% for all scenarios.

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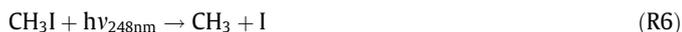
Besides a direct interest in the rate constant of the title reaction through its possible impact onto the atmospheric composition, there is also a fundamental interest: radical–radical reactions are difficult to measure and to our knowledge, the reaction between OH radicals and alkyl-peroxy radicals has never been studied experimentally. The only estimation of the rate constant of the title reaction has been carried out by Tsang and Hampson [4]: based on analogy with the reaction of HO<sub>2</sub> with OH radicals, they recommended for the reaction between CH<sub>3</sub>O<sub>2</sub> and OH a rate constant of  $k_1 = 1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  with an estimated uncertainty of a factor of 5. In the absence of any experimental study of the title reaction, the reaction of CH<sub>3</sub>O<sub>2</sub> radicals with Cl-atoms can serve as proxy: it has been investigated several times [5–8] and its rate constant is very fast ( $\approx 1.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ), proposed reaction products are either CH<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>O (corresponding to (R1a) and (R1b)) in equal amounts [5,6], while Daële and Poulet [8] suggest (R1a) as the major channel. Biggs et al. [9] have investigated experimentally the reaction of the most simple fluorinated peroxy radical CF<sub>3</sub>O<sub>2</sub> with OH. They determined a rate constant for this reaction of  $(4.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at  $296 \pm 1 \text{ K}$  with the product probably being HO<sub>2</sub> radicals. The same reaction has also been investigated theoretically by Du and Zhang [10]: DFT calculations have shown a multitude of possible reaction products, with CF<sub>3</sub>O + HO<sub>2</sub> being the major products on the triplet surface, while the situation is more complicated on the singlet surface.

Taking into account the total lack of any experimental or theoretical study of alkyl-peroxy radicals with OH radicals and their potential impact in low NO<sub>x</sub> environments, we have investigated the reaction of the most simple alkyl-peroxy radical, CH<sub>3</sub>O<sub>2</sub>, with OH.

## 2. Experimental setup

The experimental setup has been described in detail in earlier papers [11,12], a recent improvement on the continuous wave Cavity Ring Down Spectrometer (cw-CRDS) system has been described by Votava et al. [13]. Briefly, the setup consists of the photolysis cell, the photolysis laser (Lambda Physic LPX 202i), the cw-CRDS system, and the high repetition rate (10 kHz) Laser Induced Fluorescence (LIF) system [14].

CH<sub>3</sub>O<sub>2</sub> radicals were generated by the 248 nm photolysis of CH<sub>3</sub>I in the presence of O<sub>2</sub>:



Absolute time-resolved CH<sub>3</sub>O<sub>2</sub> concentration profiles have been measured at one of the most intense absorption peaks of the  $\nu_{12}$  – transition of the A←X band at  $7489.16 \text{ cm}^{-1}$  using the absorption cross section such as obtained in a recent work in our laboratory ( $\sigma = 3.40 \times 10^{-20} \text{ cm}^2$  independent of pressure) [15]. Ring-down times were converted to CH<sub>3</sub>O<sub>2</sub> concentrations using the following equation:

$$[\text{CH}_3\text{O}_2] = \frac{R_L}{c \times \sigma} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

where  $R_L$  is the ratio between the cavity length  $L$ , i.e., the distance between the two cavity mirrors (82 cm), and the length  $L_A$  over which the absorber is present (in our case the overlap of photolysis beam and absorption path, 28.7 cm),  $c$  is the speed of light. Finally,  $\tau_0$  and  $\tau$  are the ring-down times in the absence (before the photolysis pulse) and in the presence (after the photolysis pulse) of CH<sub>3</sub>O<sub>2</sub>, respectively.

OH radicals were co-generated by the simultaneous photolysis of an appropriate precursor: in most experiments, O<sub>3</sub> has been photolysed in the presence of H<sub>2</sub>O:



whereby O<sub>3</sub> is generated continuously by a commercial ozone generator (UVP–SOG 2) through photolysis of O<sub>2</sub> by a mercury lamp, leading to O(<sup>3</sup>P) atoms, which in turn recombine with O<sub>2</sub> leading to O<sub>3</sub>. The major fraction of O(<sup>1</sup>D), generated within the photolysis reactor, will be quenched by collision mostly with O<sub>2</sub>, leading to O(<sup>3</sup>P):



The possible influence of these O(<sup>3</sup>P) on the OH-decays will be discussed further down. In a few complementary experiments, H<sub>2</sub>O<sub>2</sub> photolysis at 248 nm, known as a clean OH-source [16,17], has been used as a precursor, thus excluding possible complications due to O(<sup>3</sup>P) chemistry. Relative time-resolved OH radical concentration profiles were detected by high repetition rate LIF (10 kHz) [14]. OH is excited in the (1–0) vibrational band of the A–X electronic transition at around 282 nm and the fluorescence is collected perpendicular to the laser beams through an interference filter at  $310 \pm 20 \text{ nm}$  with a photomultiplier and a Boxcar integrator (EG&G Model 412B).

All experiments were carried out at 294 K and at two different total pressures, 50 and 100 Torr. Total gas flows were 306 and  $640 \text{ cm}^3 \text{ min}^{-1}$  at 50 and 100 Torr, respectively. Such flows assured a renewal of the gas mixture between two photolysis laser shots (repetition rate being 0.2 Hz). The different gases were introduced into the reactor as stabilized flows using calibrated flow controllers (Bronkhorst and Tylan) and the total pressure was kept constant using a pressure controller (Leybold–Heraeus MR16) installed at the exit of the reactor. Helium (Praxair, 6.0) and O<sub>2</sub> (Praxair, 4.5) were used without further purification, H<sub>2</sub>O was admitted to the cell by bubbling a fraction of the main helium flow through a bubbler filled with ultrapure H<sub>2</sub>O, CH<sub>3</sub>I (Aldrich, 99%) was prepared as a 1% mixture in helium in darkened glass bulbs. At 50/100 Torr total pressure, the concentrations were: [O<sub>2</sub>] =  $5.1/2.8 \times 10^{17} \text{ cm}^{-3}$ , [H<sub>2</sub>O] =  $2.5/7.6 \times 10^{15} \text{ cm}^{-3}$  and [CH<sub>3</sub>I] has been varied for both pressures between  $(2.4\text{--}6) \times 10^{14} \text{ cm}^{-3}$ . The laser energy was varied between 13 and  $22 \text{ mJ cm}^{-2}$ , leading to initial CH<sub>3</sub>O<sub>2</sub> concentrations between 3 and  $13 \times 10^{12} \text{ cm}^{-3}$ . Some experiments have been carried out to verify the concordance of the employed absorption cross section of CH<sub>3</sub>O<sub>2</sub> with the results from our earlier measurements, carried out at higher CH<sub>3</sub>O<sub>2</sub> concentrations [15]: for these experiments, CH<sub>3</sub>O<sub>2</sub> concentrations of up to  $40 \times 10^{12} \text{ cm}^{-3}$  have been used.

For experiments with H<sub>2</sub>O<sub>2</sub> the precursor was introduced into the reactor by bubbling a fraction of the main helium flow through a 50% solution of H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O. From the OH decay in absence of CH<sub>3</sub>I, the H<sub>2</sub>O<sub>2</sub> concentration was estimated to be  $2.5 \times 10^{13} \text{ cm}^{-3}$ , leading to initial OH-concentrations of around  $1 \times 10^{11} \text{ cm}^{-3}$ .

For O<sub>3</sub>-experiments, a rough estimate of the initial O<sub>3</sub> and O(<sup>3</sup>P) concentration can be obtained from OH-decays in the absence of CH<sub>3</sub>I ( $\approx 50$  and  $180 \text{ s}^{-1}$  at 100 and 50 Torr, respectively). Under our typical photolysis energies ( $30 \text{ mJ cm}^{-2}$ ), around one third of the initial O<sub>3</sub> will be photolysed. Under these conditions the major sink for OH-radicals becomes the reaction with O(<sup>3</sup>P)



( $k_{10} = 3.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ), together with minor contributions from the much slower reaction with O<sub>3</sub>



( $k_{11} = 7.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ) and diffusion out of the photolysis volume ( $\approx 5$  and  $15 \text{ s}^{-1}$  at 100 and 50 Torr, respectively [18]). Therefore, an  $\text{O}(^3\text{P})$  concentration of around  $1/5 \times 10^{12} \text{ cm}^{-3}$  can be estimated for the experiments at 100/50 Torr, respectively, leading to initial  $\text{O}_3$  concentrations of around  $3/15 \times 10^{12} \text{ cm}^{-3}$  at 100/50 Torr, respectively. Only a few percent of the initial  $\text{O}(^1\text{D})$  will be converted to OH radicals under our conditions (depending on  $\text{H}_2\text{O}$  and  $\text{O}_2$  concentrations), leading to low OH-concentrations compared to  $\text{CH}_3\text{O}_2$ .

However,  $\text{O}(^3\text{P})$  has no impact on the OH decays in the presence of  $\text{CH}_3\text{O}_2$  because (a) OH decays are much faster under these conditions and (b)  $\text{O}(^3\text{P})$  will react predominantly with  $\text{CH}_3\text{I}$  under these conditions:



(R12) has been studied several times [19–21] and consistent rate constants between  $k_{12} = (1.7 \text{ and } 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  were found, leading to pseudo-first order rates that are fast on the time scale of our OH decays. The consequence of pathway (a) is, under our conditions, formation of additional  $\text{CH}_3\text{O}_2$  radicals with a branching ratio of 0.44 [20], but also a rapid formation of IO. The possible role of IO in our reaction system will be discussed further down. Pathway (b) leads to a rise of the OH-concentration in the first 300  $\mu\text{s}$ .

### 3. Results and discussion

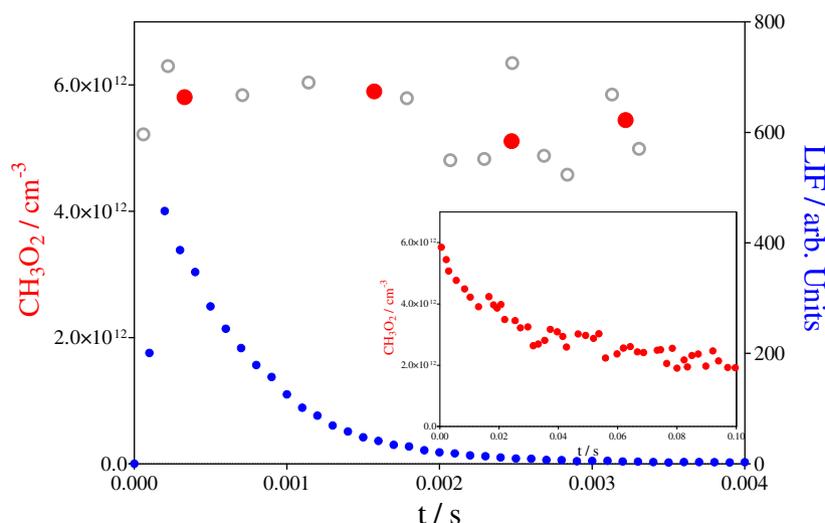
$\text{CH}_3$  radicals are generated through the photolysis of  $\text{CH}_3\text{I}$  and are converted to  $\text{CH}_3\text{O}_2$  radicals through reaction (R7) within a few 10  $\mu\text{s}$  under our experimental conditions. The rate constant  $k_8$  has been measured at low pressure (1–6 Torr helium and argon) by Selzer and Bayes [22], while the high pressure limit has been determined by Fernandes et al. [23]. From these values,  $k_7$  under our conditions can be estimated to  $k_7 = 1.4/2.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , i.e.  $k_7' = 7.2/5.9 \times 10^4 \text{ s}^{-1}$  for 50/100 Torr He, respectively. As it turned out that the rate constant  $k_1$  is extremely fast, low initial

**Table 1**  
Reaction mechanism used to simulate  $\text{CH}_3\text{O}_2$  and OH profiles.

Number	Reaction	Rate constant	Refs.
1	$\text{CH}_3\text{O}_2 + \text{OH} \rightarrow \text{products}$	Varied	This Letter
4 a	$2 \text{CH}_3\text{O}_2 \rightarrow 2 \text{CH}_3\text{O} + \text{O}_2$	$1.3 \times 10^{-13}$	[24]
4 b	$\rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	$2.2 \times 10^{-13}$	
5	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	$5.2 \times 10^{-12}$	[24]
6	$\text{CH}_3\text{I} + h\nu_{248 \text{ nm}} \rightarrow \text{CH}_3 + \text{I}$		
7	$\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}$	$1.4/2.1 \times 10^{-13}$	[22,23]
10	$\text{OH} + \text{O}(^3\text{P}) \rightarrow \text{O}_2 + \text{H}$	$3.5 \times 10^{-11}$	[35]
11	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$7.3 \times 10^{-14}$	[35]
12 a	$\text{O}(^3\text{P}) + \text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{OI}$	$7.5 \times 10^{-12}$	[20]
12 b	$\rightarrow \text{OH} + \text{CH}_2\text{I}$	$2.7 \times 10^{-12}$	
12 c	$\rightarrow \text{products}$	$7.3 \times 10^{-12}$	
13	$\text{O}(^3\text{P}) + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}_2$	$4.3 \times 10^{-11}$	[25]
14	$\text{CH}_3\text{O}_2 + \text{I} \rightarrow \text{CH}_3\text{O}_2\text{I}$	$2 \times 10^{-11}$	[27]
15	$\text{CH}_3\text{O}_2 + \text{I} \rightarrow \text{CH}_3\text{O}_2 + \text{I}_2$	$1.5 \times 10^{-10}$	[27]
16	$\text{CH}_3\text{O}_2 + \text{OI} \rightarrow \text{products}$	$3.4 \times 10^{-12}$	[30]
17	$\text{CH}_3 + \text{CH}_3\text{O}_2 \rightarrow 2 \text{CH}_3\text{O}$	$9.1 \times 10^{-11}$	[36]
18	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$1.9 \times 10^{-15}$	[24]
19	$\text{CH}_3\text{O} + \text{CH}_2\text{O} \rightarrow \text{products}$	$2.3 \times 10^{-14}$	[37]
20	$2 \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.7 \times 10^{-12}$	[35]
21	$2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	$6 \times 10^{-11}$	[38]
22	$\text{OH} + \text{I}_2 \rightarrow \text{IOH} + \text{I}$	$2.1 \times 10^{-10}$	[39]
23	$\text{O}(^3\text{P}) + \text{O}_3 \rightarrow 2 \text{O}_2$	$8 \times 10^{-15}$	[35]
24	$\text{O}(^3\text{P}) + \text{O}_2 (+\text{M}) \rightarrow \text{O}_3 (+\text{M})$	$3.36 \times 10^{-34}$	[40]

$\text{CH}_3$  concentrations were generated in these experiments such that the OH radicals decayed on a suitable time scale, i.e., pseudo-first order decays on the order of a few 1000  $\text{s}^{-1}$  ( $[\text{CH}_3\text{O}_2]_{0,\text{max}} = 1.3 \times 10^{13} \text{ cm}^{-3}$ , see below). Therefore, other radical–radical reactions that might change the initial composition of the gas mixture (such as  $\text{CH}_3 + \text{CH}_3\text{O}_2$  or  $\text{CH}_3 + \text{CH}_3$ ) are slow compared to (R7) and can be neglected: a model shows, that under our conditions the  $\text{CH}_3\text{O}_2$  concentration reaches its maximum after 6/15  $\mu\text{s}$  at 50/100 Torr and that around 96%/92% of the initial  $\text{CH}_3$  radicals have been converted to  $\text{CH}_3\text{O}_2$ , the remaining 4%/8% being converted to  $\text{C}_2\text{H}_6$  or  $\text{CH}_3\text{O}$ , whereby  $\text{CH}_3\text{O}$  will be converted to  $\text{CH}_2\text{O}$  and  $\text{HO}_2$ . The latter radical reacts fast with OH, however it has no impact on the OH decay mostly due to the delayed formation compared to the OH decays, but also due to their much lower concentration compared to  $\text{CH}_3\text{O}_2$  radicals.

Figure 1 shows a typical example of simultaneously measured OH and  $\text{CH}_3\text{O}_2$  traces. The time resolution of the OH-decay is 100  $\mu\text{s}$ , corresponding to the repetition rate of the fluorescence

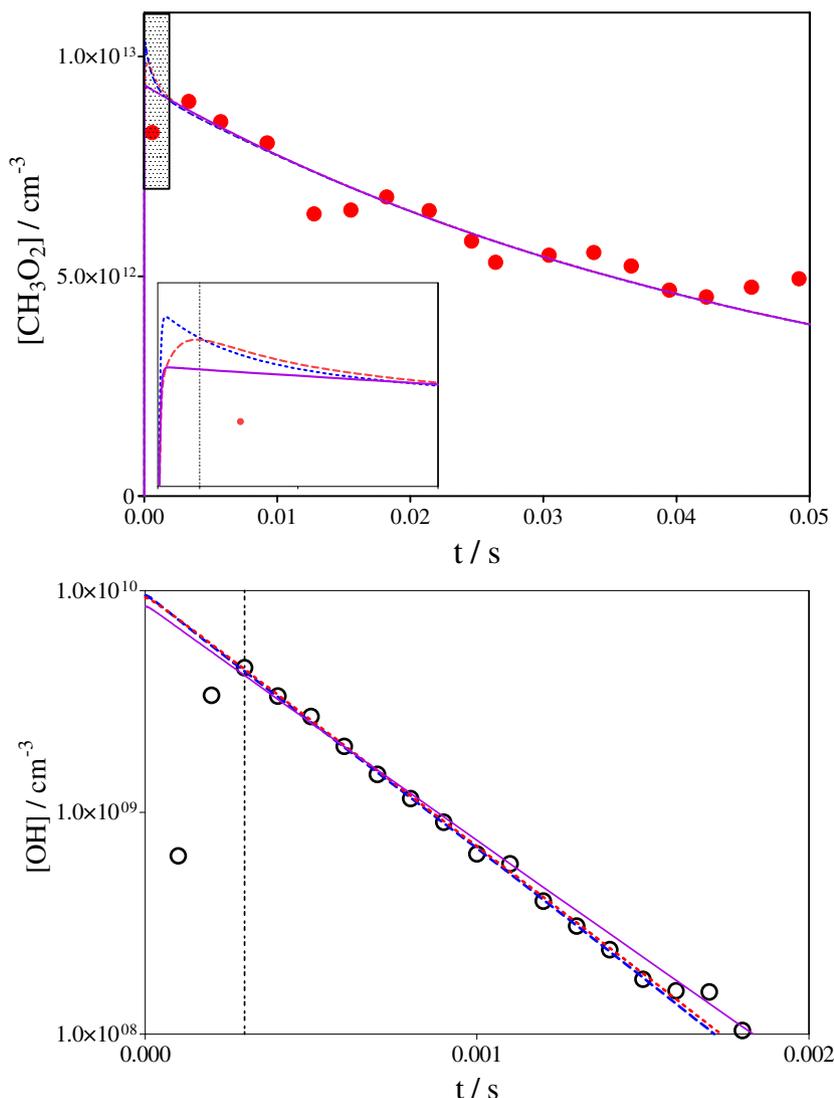
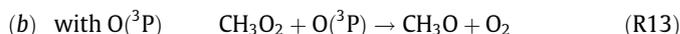


**Figure 1.** Red and open gray dots (left y-axis): absolute  $\text{CH}_3\text{O}_2$  concentrations from cw-CRDS measurements; grey dots are raw data from individual ring-down events, red dots are obtained by averaging over a time window of 1 ms. Insert shows  $\text{CH}_3\text{O}_2$  decay over 100 ms. Blue dots: relative OH concentrations from simultaneous LIF measurements (right y-scale). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

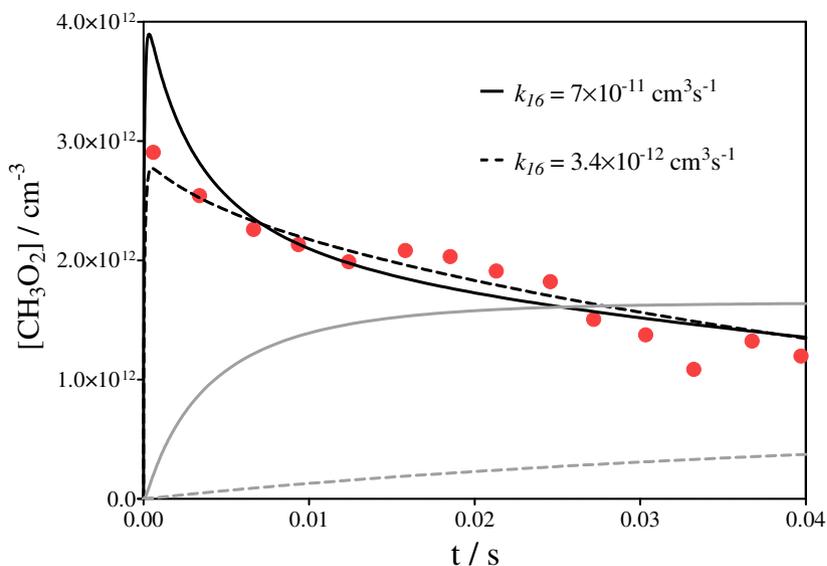
excitation laser. OH-decays become exponential only after around 300  $\mu\text{s}$  following the photolysis pulse, the initial rise is due to OH-formation in (R12b). The time resolution of the  $\text{CH}_3\text{O}_2$  decay is random due to the synchronization mode of the experimental setup [12]: raw data from individual ring down events are shown as open grey dots in Figure 1, while the red dots represent the average of ring down events having occurred within a time window of 1 ms. The insert shows the  $\text{CH}_3\text{O}_2$  decay on a longer time scale (100 ms) and it can be seen that the  $\text{CH}_3\text{O}_2$  concentration seems nearly stable on the time scale of the OH decay. However, using a simple extrapolation of the  $\text{CH}_3\text{O}_2$  concentration to  $t=0$  s in order to extract the rate constant of the title reaction from the pseudo-first order decays of the OH profile bears the risk, that rapid side reactions altering the  $\text{CH}_3\text{O}_2$  concentration at short times remain unaccounted for. On the other hand, the random time resolution makes it very tedious to obtain  $\text{CH}_3\text{O}_2$  decays with a time resolution high enough to unravel details of its concentration-time profile on the time scale of the OH-decays. Therefore,  $\text{CH}_3\text{O}_2$  decays have been simulated by a model taking into account secondary chemistry with the goal of retrieving the  $\text{CH}_3\text{O}_2$  concentration actually present during the short time window of the

corresponding OH decay. The complete model used for simulating the concentration–time profiles is given in Table 1, and the rate constant of (R1) has been extracted in two steps: in a first step, the  $\text{CH}_3\text{O}_2$  profile has been simulated on a time scale adapted to the CRDS measurements (up to 30 ms). The initial  $\text{CH}_3\text{I}$  and  $\text{O}_2$  concentrations were obtained from pressure and flow meter readings,  $\text{O}_3$  and  $\text{O}(^3\text{P})$  concentrations were estimated as explained above. Only the (identical) initial concentrations of  $\text{CH}_3$  radicals and I-atoms were varied such that the experimental  $\text{CH}_3\text{O}_2$  concentration was best reproduced over the first 30 ms. Once the initial radical concentrations were determined, the corresponding OH decay was simulated on a shorter time scale (2–5 ms, depending on the  $\text{CH}_3\text{O}_2$  concentration): only the rate constant of the title reaction,  $k_1$ , was adjusted such that the corresponding experimental OH decay was best reproduced.

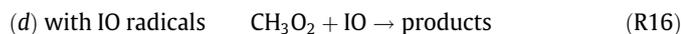
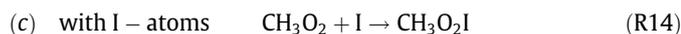
Possible side reactions that could alter the  $\text{CH}_3\text{O}_2$  concentration on a short time scale are:



**Figure 2.** Upper panel:  $\text{CH}_3\text{O}_2$  concentration time profile, insert shows zoom of the shaded area, representing the same time scale than the OH-decay in the lower panel. Lower panel: OH decay, open dots are experimental LIF intensities, normalized to an estimated initial OH concentration of  $10^{10} \text{ cm}^{-3}$ , the horizontal dashed line in the insert upper panel and in the lower panel indicates 300  $\mu\text{s}$ . The full line presents a model without secondary chemistry, dotted blue line includes I-chemistry (R14) and (R15), dashed red line is the full model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Figure 3.** Simulation showing the impact of the rate constant of (R16) on the  $\text{CH}_3\text{O}_2$  profile, full grey and dashed grey lines show the concentration profile of the product of (R16).



(a) The initial  $\text{CH}_3\text{O}_2$  concentrations being very low, the self-reaction of the  $\text{CH}_3\text{O}_2$  radicals with a recommended rate constant [24] of  $k_4 = 3.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  is also very slow and can be safely neglected on the time scale of the OH decays.

(b) The reaction of  $\text{CH}_3\text{O}_2$  with  $\text{O}(^3\text{P})$ -atoms has been studied by Zellner et al. [25] and a rate constant of  $k_{13} = (4.3 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  has been found, which leads under our conditions to pseudo-first order decays of 120–400  $\text{s}^{-1}$ , slow compared to the OH decays.

(c) The reaction of  $\text{CH}_3\text{O}_2$  radicals with I-atoms has first been mentioned by Jenkin and Cox [26] and has more recently been studied in detail by Dillon et al. [27]. It was found that  $\text{CH}_3\text{O}_2$  radicals catalyze the recombination of I-atoms in a Chaperon-like mechanism, with the rate constant for (R15) being roughly 10 times faster than for (R14). As a consequence, the  $\text{CH}_3\text{O}_2$  concentration decreases rapidly by around 10% until the pseudo-first order rates of (R14) and (R15) are equalized. This decay occurs under our conditions within 1–2 ms, i.e., the time scale of our OH-decays, and therefore needs to be taken into account.

(d) Reaction (R16) has been studied several times: Enami et al. [28] as well as Bale et al. [29] report a rate constant of around  $7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , while Dillon et al. [27,30] have reported twice, using very different experimental setups and conditions, a rate constant 15–30 times slower (more discussion see further down).

In Figures 2 and 3 is shown the impact of (R13) to (R16) on the  $\text{CH}_3\text{O}_2$  concentration–time profile. The upper panel of Figure 2 presents a  $\text{CH}_3\text{O}_2$  profile for an experiment with a rather high initial radical concentration, the insert shows a zoom of the shaded area and represents the time scale of the OH decay, depicted on a logarithmic scale in the lower panel. The vertical dashed line indicates 300  $\mu\text{s}$ , the time when the OH decays became exponential. Three different simulations of the mechanism in Table 1 are shown, which all reproduce very well the  $\text{CH}_3\text{O}_2$  concentration at longer time scales. Differences however are visible in the zoom: (a) the lower, full line represents a model with the I and  $\text{O}(^3\text{P})$  concentra-

tions set to 0, i.e., no secondary chemistry is taken into account; (b) the dashed line takes into account I-chemistry, i.e., the I-atom concentration was set to the same value as the  $\text{CH}_3$  concentration; (c) the dotted line finally represents the full model with additionally the  $\text{O}(^3\text{P})$  concentration set to the estimated value. In order to reproduce  $\text{CH}_3\text{O}_2$  at longer time scales, the initial  $\text{CH}_3$  and I-concentrations need to be adjusted between the different simulations by 10–15%. Fitting of the corresponding OH-decay leads to identical results for  $k_1$  for (b) and (c), while neglecting any secondary chemistry would ask for an increase in the rate constant of the title reaction of around 10% in order to make up for the lower  $\text{CH}_3\text{O}_2$  concentration: to illustrate the difference, all simulations in the lower panel use the same rate constant  $k_1$ , i.e., the simulation (a) was not optimized for reproducing the OH decay.

Figure 3 shows the impact of IO chemistry (R16): a  $\text{CH}_3\text{O}_2$  profile with low initial radical, but high  $\text{O}(^3\text{P})$  concentration is depicted, conditions under which (R16) has the highest impact. The full model from Table 1 is run by using the two rate constants found in the literature: the full line represents the model with  $k_{16} = 7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  such as proposed by Enami et al. [28] and Bale et al. [29], while the dashed line represents a model using  $k_{16} = 3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , the most recent value from Dillon et al. [30]. Again, the initial  $\text{CH}_3$ - and I-concentrations have been adjusted such that the  $\text{CH}_3\text{O}_2$  concentration is best reproduced on longer time scales. It can be seen that under the conditions of this experiment the higher value for  $k_{16}$  leads to a strong decrease of the  $\text{CH}_3\text{O}_2$  concentration on the time scale of typical OH-decays (few ms) and would therefore influence the retrieved value for  $k_1$ . However, such high rate constant for (R16) is not in agreement with the experimental  $\text{CH}_3\text{O}_2$  profile. The lower value for  $k_{16}$  influences the  $\text{CH}_3\text{O}_2$  concentration only at long reaction times as can be seen from the slow rise of the product of (R16), represented by the grey lines. It has thus no impact on the retrieved value for  $k_1$ .

The rate constants such as obtained by fitting  $\text{CH}_3\text{O}_2$  and OH decays to the full model, are summarized in Table 2 and presented in Figure 4 as a function of the initial radical concentration. No systematic trend is observed for the retrieved rate constant between the two different sets of experimental conditions (different pressure,  $\text{O}(^3\text{P})$  and  $\text{O}_3$  concentration), which can be taken as another indication, that (R16) is too slow to influence the  $\text{CH}_3\text{O}_2$

concentration profile on short time scales. The average value of the rate constant for (R1), obtained from fitting all experiments to the full model using the rate constants shown in Table 1, is  $k_1 = (2.80 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , with the error being statistical only (95% confidence interval), but other systematic errors need to be considered. Few experiments have been carried out using  $\text{H}_2\text{O}_2$  as precursor, thus avoiding complications due to (R13) and (R16): a rate constant in excellent agreement with the one obtained using  $\text{O}_3$  as an OH-precursor has been found.

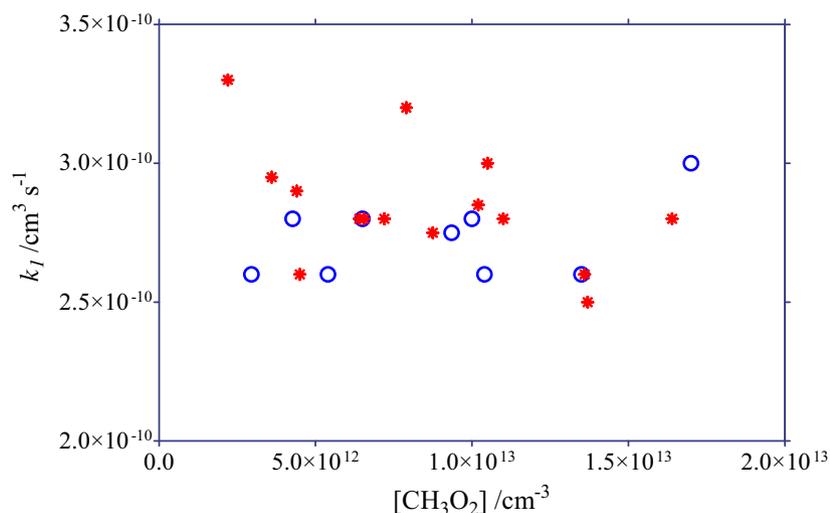
However, with both precursors, the rate constant fully depends on the reliable determination of the  $\text{CH}_3\text{O}_2$  concentration, any systematic error directly returns a proportional error in the rate con-

stant  $k_1$ . The  $\text{CH}_3\text{O}_2$  concentration has been obtained by applying [Eq. (1)] to the time-resolved cw-CRDS measurements and thus transforming ring down times into absolute  $\text{CH}_3\text{O}_2$  concentrations. The absorption cross section ( $3.40 \times 10^{-20} \text{ cm}^2$  at  $7489.16 \text{ cm}^{-1}$ ) has recently been determined in our laboratory [15] in the same experimental setup, using the same method for generating  $\text{CH}_3\text{O}_2$  radicals. The absorption cross section was obtained from a kinetic analysis of the  $\text{CH}_3\text{O}_2$  decay under conditions where self-reaction is preponderant, i.e., high concentrations. Indeed, considering the known rate constant of the self-reaction permits to retrieve the absolute initial  $\text{CH}_3\text{O}_2$  concentration. This method has already been used earlier in our group [31] for the determination of the absorp-

**Table 2**

Results of fitting individual decays of all  $\text{O}_3$  experiments to the mechanism such as shown in Table 1. The error on the average value is statistical only (95% confidence interval).

$\text{CH}_3\text{I}/10^{14} \text{ cm}^{-3}$	$E/\text{mJ cm}^{-2}$	$[\text{CH}_3]_0 = [\text{I}]_0/10^{12} \text{ cm}^{-3}$	$k_1/10^{-10} \text{ cm}^3 \text{ s}^{-1}$
$p = 50 \text{ Torr}$ , $[\text{O}_2] = 5 \times 10^{17} \text{ cm}^{-3}$ , $[\text{O}_3] \approx 1.5 \times 10^{13} \text{ cm}^{-3}$ , $\text{O}(^3\text{P}) \approx 5 \times 10^{12} \text{ cm}^{-3}$			
7.9	21	18.0	3.0
4.9	21	14.0	2.8
3.1	21	8.4	2.8
1.8	21	4.3	2.8
6.7	13.4	13.5	2.6
5.3	13.4	10.4	2.6
3.1	13.4	5.4	2.6
1.8	13.4	3.0	2.6
4.9	13.4	9.4	2.75
$p = 100 \text{ Torr}$ , $[\text{O}_2] = 1.9 \times 10^{17} \text{ cm}^{-3}$ , $[\text{O}_3] \approx 0.3 \times 10^{13} \text{ cm}^{-3}$ , $\text{O}(^3\text{P}) \approx 1 \times 10^{12} \text{ cm}^{-3}$			
6.6	13.4	10.5	3.0
5.4	13.4	7.9	3.2
4.2	13.4	6.4	2.8
3.0	13.4	4.4	2.9
1.7	13.4	2.2	3.3
1.7	20	3.6	2.95
1.7	22	4.5	2.6
3.0	22	7.2	2.8
3.0	18	6.6	2.8
4.2	18	8.8	2.75
4.2	22	10.2	2.85
5.4	22	13.6	2.6
5.4	18	11.0	2.8
6.6	18	13.7	2.5
6.6	22	16.4	2.8
Average:			$(2.80 \pm 0.06) \times 10^{-10}$



**Figure 4.** Rate constants for the title reaction such as obtained from the simulations of the individual experiments to the full model from Table 1 as a function of initial radical concentration. Open symbols are from experiments at 50 Torr with relatively high  $\text{O}_3$  and  $\text{O}(^3\text{P})$  concentrations (upper part of Table 2), red stars are results from experiments at 100 Torr, containing comparably lower  $\text{O}_3$  and  $\text{O}(^3\text{P})$  concentrations (lower part of Table 2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tion cross sections of HO<sub>2</sub>, which has later been confirmed using a different method by Tang et al. [32]. The cross section for CH<sub>3</sub>O<sub>2</sub> determined in our group [15] is 2–3 times larger than earlier determinations by Pushkarsky et al. [33] and Atkinson and Spillman [34] using the same method, but plausible arguments have been presented by Farago et al. for this disagreement. A major source of uncertainty in the determination of the CH<sub>3</sub>O<sub>2</sub> concentration is the uncertainty in the rate constant for the self-reaction, on which is based the determination of the absorption cross section in all three experiments. An uncertainty of 30% is given by the IUPAC committee for the rate constant  $k_4$  [24], translating into the same uncertainty for the CH<sub>3</sub>O<sub>2</sub> concentration. Another estimated uncertainty of 20% is added in order to take into account some dubiety remaining in the influence of secondary chemistry (R13) to (R16) on the CH<sub>3</sub>O<sub>2</sub> concentration at short reaction times, leading to a final uncertainty of the rate constant of ±50%:

$$k_1 = (2.8 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{R17})$$

This very fast rate constant suggests that the impact of the reaction of peroxy radicals with OH radicals is not negligible under certain, remote condition and might be even more important than shown by Archibald et al., who used rate constants of up to  $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  in his model. It should be noted however, that a lower absorption cross section for CH<sub>3</sub>O<sub>2</sub> such as obtained by Pushkarsky et al. or Atkinson and Spillman would result in a lower rate constant: another determination of the absorption cross section of CH<sub>3</sub>O<sub>2</sub> radicals would be most welcome. More laboratory studies are also needed to determine the rate constants of larger peroxy radicals with OH, and also, if possible, to determine the reaction products. High level *ab initio* calculations should be carried out in order to understand the mechanism of this very fast reaction and to determine the reaction pathway and product yields.

#### 4. Conclusion

The rate constant of the reaction between the methylperoxy radical CH<sub>3</sub>O<sub>2</sub>, and the OH radical has been measured for the first time. Relative OH decays have been obtained by high repetition rate LIF in the presence of excess CH<sub>3</sub>O<sub>2</sub>. The absolute concentration of CH<sub>3</sub>O<sub>2</sub> was measured simultaneously by time resolved cw-CRDS in the near IR. A very fast rate constant of  $(2.8 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , independent of pressure between 50 and 100 Torr, has been obtained. With such a fast rate constant, the reaction of CH<sub>3</sub>O<sub>2</sub> radicals (and peroxy radicals in general) with OH radicals will be needed to be implemented into atmospheric chemistry models, as it will have non-negligible impact on the composition of the atmosphere especially in remote environments where NO<sub>x</sub> concentrations are low and the lifetime of peroxy radicals is long.

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