

# Kinetics and Product Branching Ratio Study of the $\text{CH}_3\text{O}_2$ Self-Reaction in the Highly Instrumented Reactor for Atmospheric Chemistry

Published as part of *The Journal of Physical Chemistry virtual special issue "Advances in Atmospheric Chemical and Physical Processes"*.

Lavinia Onel, Alexander Brennan, Freja F. Østerstrøm, Ellie Cooke, Lisa Whalley, Paul W. Seakins, and Dwayne E. Heard\*



Cite This: *J. Phys. Chem. A* 2022, 126, 7639–7649



Read Online

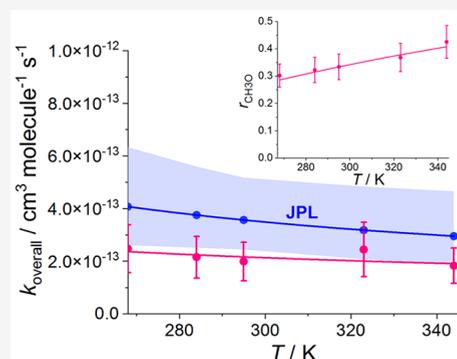
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** The fluorescence assay by gas expansion (FAGE) method for the measurement of the methyl peroxy radical ( $\text{CH}_3\text{O}_2$ ) using the conversion of  $\text{CH}_3\text{O}_2$  into methoxy radicals ( $\text{CH}_3\text{O}$ ) by excess  $\text{NO}$ , followed by the detection of  $\text{CH}_3\text{O}$ , has been used to study the kinetics of the self-reaction of  $\text{CH}_3\text{O}_2$ . Fourier transform infrared (FTIR) spectroscopy has been employed to determine the products methanol and formaldehyde of the self-reaction. The kinetics and product studies were performed in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) in the temperature range 268–344 K at 1000 mbar of air. The product measurements were used to determine the branching ratio of the reaction channel forming methoxy radicals,  $r_{\text{CH}_3\text{O}}$ . A value of  $0.34 \pm 0.05$  (errors at  $2\sigma$  level) was determined for  $r_{\text{CH}_3\text{O}}$  at 295 K. The temperature dependence of  $r_{\text{CH}_3\text{O}}$  can be parametrized as  $r_{\text{CH}_3\text{O}} = 1/\{1 + [\exp(600 \pm 85)/T]/(3.9 \pm 1.1)\}$ . An overall rate coefficient of the self-reaction of  $(2.0 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K was obtained by the kinetic analysis of the observed second-order decays of  $\text{CH}_3\text{O}_2$ . The temperature dependence of the overall rate coefficient can be characterized by  $k_{\text{overall}} = (9.1 \pm 5.3) \times 10^{-14} \times \exp((252 \pm 174)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The found values of  $k_{\text{overall}}$  in the range 268–344 K are  $\sim 40\%$  lower than the values calculated using the recommendations of the Jet Propulsion Laboratory and IUPAC, which are based on the previous studies, all of them utilizing time-resolved UV-absorption spectroscopy to monitor  $\text{CH}_3\text{O}_2$ . A modeling study using a complex chemical mechanism to describe the reaction system showed that unaccounted secondary chemistry involving Cl species increased the values of  $k_{\text{overall}}$  in the previous studies using flash photolysis to initiate the chemistry. The overestimation of the  $k_{\text{overall}}$  values by the kinetic studies using molecular modulation to generate  $\text{CH}_3\text{O}_2$  can be rationalized by a combination of underestimated optical absorbance of  $\text{CH}_3\text{O}_2$  and unaccounted  $\text{CH}_3\text{O}_2$  losses to the walls of the reaction cells employed.

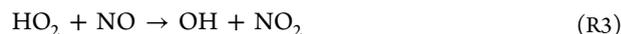


## INTRODUCTION

Methyl peroxy ( $\text{CH}_3\text{O}_2$ ) radicals are key species in atmospheric oxidation<sup>1</sup> and the combustion of volatile organic compounds.<sup>2,3</sup> The chemistry of  $\text{CH}_3\text{O}_2$  in the troposphere is typically dominated by the reaction with  $\text{NO}$ , particularly in environments influenced by anthropogenic  $\text{NO}_x$  emissions (reaction R1). The reaction is a critical step in the tropospheric production of ozone in the presence of  $\text{NO}$  and converts  $\text{NO}$  into  $\text{NO}_2$ :



The subsequent reaction of  $\text{CH}_3\text{O}$  with  $\text{O}_2$  produces  $\text{HO}_2$ , which then oxidizes another  $\text{NO}$  to  $\text{NO}_2$ :



During the daytime the  $\text{NO}_2$  photolysis is the dominant tropospheric source of  $\text{O}_3$ . In addition, the  $\text{CH}_3\text{O}_2 + \text{NO}$  reaction leads to the propagation of  $\text{HO}_x$  and  $\text{NO}_x$  radical chains. However, under low  $\text{NO}_x$  levels the self-reaction of  $\text{CH}_3\text{O}_2$  and the reactions of  $\text{CH}_3\text{O}_2$  with  $\text{HO}_2$  and other organic peroxy ( $\text{RO}_2$ ) species are significant losses of  $\text{CH}_3\text{O}_2$

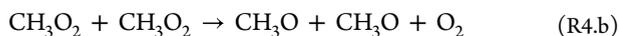
Received: July 13, 2022

Revised: September 13, 2022

Published: October 13, 2022



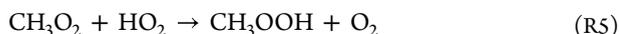
and terminate the radical chain. The  $\text{CH}_3\text{O}_2$  self-reaction occurs through two channels, reactions R4.a and R4.b:<sup>4</sup>



The methoxy radicals generated by channel R4.b subsequently react with oxygen (reaction R2) to form  $\text{CH}_2\text{O}$  and  $\text{HO}_2$ .

Despite its importance, the reported values for the rate coefficient of reaction R4,  $k_4$ , at room temperature lie in a wide range from  $(2.7\text{--}5.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>5</sup> with IUPAC<sup>5</sup> and the Jet Propulsion Laboratory (JPL)<sup>6</sup> giving 20–40% and 40–50%, respectively, uncertainties at the  $2\sigma$  level for  $k_4$  in the temperature range 270–350 K. The previous kinetic studies used either the flash photolysis (FP) technique<sup>7–11</sup> or the molecular modulation (MM) method<sup>12–14</sup> to generate  $\text{CH}_3\text{O}_2$  radicals, which were coupled to time-resolved UV-absorption spectroscopy to detect  $\text{CH}_3\text{O}_2$  at fixed wavelengths in the range  $\sim 210\text{--}270 \text{ nm}$  (typically at 250 nm). As UV-absorption is a relatively insensitive technique, the detection limits of  $\text{CH}_3\text{O}_2$  were high, for example around  $4 \times 10^{12} \text{ molecules cm}^{-3}$ ,<sup>8,11</sup> and the UV-absorption studies used high initial concentrations of  $\text{CH}_3\text{O}_2$ ,  $10^{13}\text{--}10^{14} \text{ molecules cm}^{-3}$  orders of magnitude.<sup>7–11</sup>

The kinetic studies of the  $\text{CH}_3\text{O}_2$  self-reaction used photolytic mixtures of  $\text{CH}_4/\text{Cl}_2/\text{O}_2$  to generate  $\text{CH}_3\text{O}_2$ .<sup>7–14</sup>  $\text{CH}_3\text{O}$  formed by the reaction R4.b is rapidly removed via the reaction with  $\text{O}_2$  (reaction R2) in high concentrations ( $10^{17}\text{--}10^{18} \text{ molecules cm}^{-3}$  orders of magnitude)<sup>7–14</sup> to generate  $\text{HO}_2$ , which quickly reacts further with another  $\text{CH}_3\text{O}_2$  radical (reaction R5).



As each  $\text{HO}_2$  radical consumes rapidly one  $\text{CH}_3\text{O}_2$  species on the time scale of the  $\text{CH}_3\text{O}_2$  self-reaction, the determination of the overall rate coefficient of the reaction R4,  $k_4$ , requires knowledge of the branching ratios for reaction R4 (eq 1)<sup>7,11</sup>

$$k_{\text{obs}} = k_4(1 + r_{\text{CH}_3\text{O}}) \quad (1)$$

where  $k_{\text{obs}}$  is the second-order observed rate coefficient and  $r_{\text{CH}_3\text{O}}$  is the branching ratio of the reaction channel producing  $\text{CH}_3\text{O}$  (reaction R4.b).

The branching ratios in the  $\text{CH}_3\text{O}_2$  self-reaction were the subject of a number of experimental studies performed from the mid 1970s to 1990 inclusive, which were followed by the study of Tyndall et al. in 1998.<sup>15</sup> The studies used photolysis of  $\text{CH}_4/\text{Cl}_2/\text{O}_2$  or  $(\text{CH}_3)_2\text{N}_2/\text{O}_2$  and either end product detection employing mass spectrometry (MS),<sup>16</sup> GC-MS,<sup>17</sup> and infrared spectroscopy,<sup>15,18–20</sup> or kinetic measurements using time-resolved UV-absorption spectroscopy.<sup>7</sup>

Some of the early studies reported a third channel of the self-reaction leading to  $\text{CH}_3\text{OOCH}_3$  (reaction R4.c) with an insignificant contribution to the overall reaction rate coefficient at all temperatures—such as  $\leq 0.08$  at 297 K<sup>19</sup> and  $\leq 0.07$  at 298 K<sup>18</sup>—with other studies finding no evidence for any contribution of peroxide formation.<sup>15,20</sup>



IUPAC<sup>5</sup> and JPL<sup>6</sup> use the evaluation of Tyndall et al.<sup>21</sup> that recommends considering reactions R4.a and R4.b as the sole reaction channels of the self-reaction.

The majority of the branching ratios studies were carried out at room temperature<sup>15,16,18–20</sup> and resulted in a range of values

for the branching ratio of the reaction channel leading to  $\text{CH}_3\text{O}$  (reaction R4.b):  $r_{\text{CH}_3\text{O}} = 0.22\text{--}0.45$ . Tyndall et al.<sup>21</sup> revised the room temperature results to obtain  $r_{\text{CH}_3\text{O}} = 0.37 \pm 0.06$  at 298 K, which is recommended by IUPAC<sup>5</sup> and JPL<sup>6</sup>. There have been two experimental studies of the temperature dependence of the branching ratios, which were conducted over different temperature ranges.<sup>7,20</sup> Lightfoot et al.<sup>7</sup> found a positive temperature dependence for  $r_{\text{CH}_3\text{O}}$  between 388 and 573 K using flash photolysis in combination with time-resolved UV-absorption spectroscopy. Horie et al.<sup>20</sup> performed the only branching ratio experimental study covering temperatures below room temperature using matrix isolation Fourier transform infrared spectroscopy. The results were obtained from 223–333 K to show a positive temperature dependence for  $r_{\text{CH}_3\text{O}}$ . Tyndall et al.<sup>21</sup> combined the results of Lightfoot et al.<sup>7</sup> and Horie et al.<sup>20</sup> with their recommended value at 298 K,  $r_{\text{CH}_3\text{O}} = 0.37 \pm 0.06$ , and results published prior to 1990 to describe the ratio of the rate coefficients of the two reaction channels R4.a and R4.b as  $\frac{k_{4,b}}{k_{4,a}} = (26.2 \pm 6.6) \times \exp[-(1130 \pm 240)/T]$ . The evaluation of Tyndall et al.<sup>21</sup> is recommended by JPL.<sup>6</sup>

This work reports on the determination of the branching ratios and the overall rate coefficient of the  $\text{CH}_3\text{O}_2$  self-reaction in the temperature range of 268–344 K at 1000 mbar of synthetic air. The kinetic and branching ratio measurements were performed in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC). Fourier Transform Infrared (FTIR) spectroscopy was employed to monitor the time profiles of the concentrations of  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OH}$  produced by the  $\text{CH}_3\text{O}_2$  self-reaction to determine the branching ratios of the two reaction channels R4.a and R4.b.

The fluorescence assay by gas expansion (FAGE) method for the selective and sensitive detection of  $\text{CH}_3\text{O}_2$  radicals was used to study the kinetics of the self-reaction.<sup>22,23</sup> The method involves the titration of  $\text{CH}_3\text{O}_2$  to  $\text{CH}_3\text{O}$  by reaction with added NO, followed by the detection of the resultant  $\text{CH}_3\text{O}$  by off-resonant LIF with laser excitation at ca. 298 nm.<sup>22</sup> The FAGE instrument was calibrated for  $\text{CH}_3\text{O}_2$  using the 184.9 nm photolysis of water vapor in air to generate OH followed by the conversion of OH to known concentrations of  $\text{CH}_3\text{O}_2$  by reaction with  $\text{CH}_4$  and  $\text{O}_2$ .<sup>22,23</sup> The 184.9 nm photolysis of water vapor is a well-established method of FAGE calibration for OH and  $\text{HO}_2$ .<sup>24–26</sup> The FAGE method for the  $\text{CH}_3\text{O}_2$  detection has been validated previously using the direct and absolute near-IR Cavity Ring Down Spectroscopy (CRDS) method to detect  $\text{CH}_3\text{O}_2$ .<sup>23</sup>

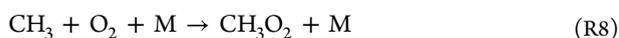
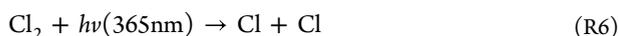
FAGE measurements were carried out in the HIRAC chamber to determine the observed rate coefficient of the  $\text{CH}_3\text{O}_2$  self-reaction,  $k_{\text{obs}}$ , at 1000 mbar and temperatures in the range of 268–344 K. Using  $k_{\text{obs}}$  and the branching ratio of the reaction channel leading to methoxy radicals,  $r_{\text{CH}_3\text{O}}$ , the overall rate coefficient of the self-reaction,  $k_4$ , was derived. This is the first kinetic study of the  $\text{CH}_3\text{O}_2$  self-reaction using a different detection method to that of UV-absorption spectroscopy.

## EXPERIMENTAL SECTION

**$\text{CH}_3\text{O}_2$  Generation in HIRAC.** The HIRAC chamber is a stainless steel cylinder with an internal volume of  $\sim 2.25 \text{ m}^3$  and has been described in detail elsewhere.<sup>22,23,27,28</sup> Four circulation fans mounted in pairs at each end of HIRAC are used to homogenize the gas mixture contained in the chamber.

The photochemistry is initiated by eight UV lamps, each of them housed in a quartz tube. The quartz tubes are mounted radially inside the chamber (aligned parallel to the chamber longitudinal axis). In order to perform experiments at temperatures different to the room temperature a thermofluid (HUBE6479 DW-therm oil) is circulated from a high capacity thermoregulator (Huber Unistat 390W) through a series of stainless steel channels welded to the outside of the chamber. To ensure that the temperature is homogeneous within the chamber, the layout of these channels is evenly distributed on the chamber outer surface and HIRAC is lagged in a 20-mm-thick expanded neoprene.

The experiments were carried out at 268, 284, 295, 323, and 344 K and 1000 mbar of synthetic air obtained by mixing high purity oxygen (BOC, > 99.999%) and nitrogen (BOC, > 99.998%) in the ratio of O<sub>2</sub>:N<sub>2</sub> = 1:4. CH<sub>4</sub> (BOC, CP grade, 99.5%) and Cl<sub>2</sub> (Sigma-Aldrich, ≥ 99.5%) were delivered to the chamber. Initial reagent concentrations in HIRAC were [CH<sub>4</sub>] = (2.0–3.0) × 10<sup>17</sup> molecules cm<sup>-3</sup> and [Cl<sub>2</sub>] = (0.3–5.5) × 10<sup>14</sup> molecules cm<sup>-3</sup>. After adding the reagents into the chamber, the lamps (Phillips, TL-D36W/BLB, λ = 350–400 nm) were turned on to generate CH<sub>3</sub>O<sub>2</sub> by Cl<sub>2</sub> photolysis at ~365 nm (reaction R6) followed by reactions R7 and R8. In the kinetic experiments the lamps were turned on for about 5 min, and then they were turned off to record the generated CH<sub>3</sub>O<sub>2</sub> kinetic decay. In the experiments performed to determine the product branching ratio the lamps were turned on to measure CH<sub>3</sub>OH and CH<sub>2</sub>O using FTIR spectroscopy for a typical time of 20 min.



**Fourier Transform Infrared (FTIR) Measurements.** An *in situ* multipass FTIR (Bruker IFS66) arrangement along the long axis of HIRAC was used to measure the concentrations of CH<sub>2</sub>O and CH<sub>3</sub>OH produced during the times with the lamps turned on. The multipass Chernin arrangement within the chamber was optimized for 72 internal reflections giving an approximate total path length of 128.5 m.<sup>27,29</sup> IR spectra were recorded every 30–60 s as the average of 30–100 scans at 1 cm<sup>-1</sup> resolution. The concentration–time profiles for CH<sub>2</sub>O and CH<sub>3</sub>OH were obtained using the absorption at around 1740 cm<sup>-1</sup> due to the stretch of the C=O bond of CH<sub>2</sub>O and at around 1030 cm<sup>-1</sup> due to the C–O stretch of CH<sub>3</sub>OH and using reference spectra taken of formaldehyde and methanol. Reference spectra were taken delivering CH<sub>2</sub>O and CH<sub>3</sub>OH in known concentrations to the chamber under the same conditions as those used for the CH<sub>3</sub>O<sub>2</sub> self-reaction experiments. The reference compound, either CH<sub>2</sub>O or CH<sub>3</sub>OH, was delivered in the vapor phase by direct heating of either liquid CH<sub>3</sub>OH or *para*-formaldehyde powder in a glass finger connected to a one liter stainless steel cylinder to achieve a gas pressure of a few mbar. Then the gas was delivered from the cylinder to the chamber using a flow of N<sub>2</sub> (p<sub>N<sub>2</sub></sub> = 2000 mbar).

The reference spectra of CH<sub>2</sub>O and CH<sub>3</sub>OH were fitted to the observed IR absorbance recorded as a function of wavelength (λ) and time (t), A<sub>obs,t</sub>, between ~1600–1900 cm<sup>-1</sup> and ~900–1120 cm<sup>-1</sup>, respectively, at each time point to determine the changes to concentrations of CH<sub>2</sub>O and

CH<sub>3</sub>OH vs time during the period of time with the lamps switched on (eq 2).

$$A_{\text{obs},t} = f_i A_{\text{ref},i(t)} \quad (2)$$

Here A<sub>ref,i(t)</sub> is the reference IR absorbance of species *i* as a function of λ and  $f_i = \frac{[i]_t}{[i]_{\text{ref}}}$ , where [i]<sub>t</sub> is the concentration of species *i* at reaction time *t* and [i]<sub>ref</sub> is the concentration of species *i* giving the reference spectrum. The species *i* is CH<sub>2</sub>O in the fit using λ ≅ 1600–1900 cm<sup>-1</sup> and CH<sub>3</sub>OH in the fit over ~900–1120 cm<sup>-1</sup>. The concentrations [i]<sub>t</sub> (*i* = CH<sub>2</sub>O or CH<sub>3</sub>OH) were then derived (eq 3).

$$[i]_t = f_i [i]_{\text{ref}} \quad (3)$$

**FAGE Instrument and Calibration for CH<sub>3</sub>O<sub>2</sub>.** Details on the HIRAC FAGE instrument are provided in previous publications.<sup>22,23,30</sup> The instrument sampled gas through a 1-mm-diameter pinhole mounted on one end of a 50-mm-i.d. flow tube at a rate of ~3 slpm. The pressure inside the sampling tube was maintained at 3.3 mbar for a chamber pressure of 1000 mbar of synthetic air. A CH<sub>3</sub>O fluorescence detection cell was integrated in the tube at ~600 mm distance from the pinhole. About 25 mm prior to the detection cell, high purity NO (BOC, N2.5 nitric oxide) was injected at 2.5 scfm using a mass flow controller (Brooks 5850S) into the center of the gas flow to convert CH<sub>3</sub>O<sub>2</sub> radicals into CH<sub>3</sub>O. CH<sub>3</sub>O radicals were subsequently detected by LIF spectroscopy, directing laser light at λ<sub>online</sub> ≅ 297.79 nm to excite the A<sup>2</sup>A<sub>1</sub>(ν<sub>3</sub>' = 3) ← X<sup>2</sup>E(ν<sub>3</sub>" = 0) transition of CH<sub>3</sub>O with a 5 kHz pulse repetition frequency through the cell at a right angle to the gas flow. The off-resonant red-shifted LIF (320–430 nm) was monitored using photon counting. The laser background was measured at a wavelength of λ<sub>online</sub> + 2.5 nm and then subtracted to obtain the fluorescence signal.

The FAGE technique requires calibration to convert the measured fluorescence signal into CH<sub>3</sub>O<sub>2</sub> concentration. The calibration procedure has been described in detail previously<sup>22,23</sup> and hence only the important points are presented here. OH radicals were generated photolyzing water vapor in synthetic air at 184.9 nm to react with methane in excess (BOC, CP grade, 99.5%) to generate CH<sub>3</sub>O<sub>2</sub>. The produced air/radical mixture was then sampled by the FAGE instrument. The concentration of CH<sub>3</sub>O<sub>2</sub> was determined using eq 4.

$$[\text{CH}_3\text{O}_2] = [\text{OH}] = [\text{H}_2\text{O}] \cdot \sigma \cdot \Phi \cdot F \cdot t \quad (4)$$

Here σ is the absorption cross section of water vapor at 184.9 nm, (7.2 ± 0.2) × 10<sup>-20</sup> cm<sup>2</sup> molecule<sup>-1</sup>,<sup>31,32</sup> Φ is the photodissociation quantum yield of OH at 184.9 nm (unity), *t* is the photolysis time, and *F* is the lamp flux at 184.9 nm, which was varied to generate a range of CH<sub>3</sub>O<sub>2</sub> radical concentrations. The product *F* × *t* was determined employing chemical actinometry.<sup>28</sup>

The FAGE calibration factor was utilized to determine [CH<sub>3</sub>O<sub>2</sub>] in the HIRAC experiments:

$$[\text{CH}_3\text{O}_2] = \frac{S_{\text{CH}_3\text{O}_2}}{C_{\text{CH}_3\text{O}_2}} \quad (5)$$

where S<sub>CH<sub>3</sub>O<sub>2</sub></sub> (counts s<sup>-1</sup> mW<sup>-1</sup>) is the recorded signal. Previous studies have shown that the FAGE sensitivity toward OH does not depend on the chamber temperature in the range 263–344 K,<sup>33</sup> and thus the calibration factor determined at a

room temperature of 295 K,  $C_{\text{CH}_3\text{O}_2} = (5.0 \pm 1.7) \times 10^{-10}$  counts  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \text{mW}^{-1}$ , was used in the kinetic analysis at all temperatures.

## RESULTS

### Product Branching Ratios in the $\text{CH}_3\text{O}_2$ Self-Reaction.

To determine the branching ratios in the  $\text{CH}_3\text{O}_2$  self-reaction (reactions R4.a and R4.b) the time profiles of the concentrations of the self-reaction products  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$  generated by turning the lamps on were recorded employing FTIR spectroscopy at a time intervals of 30–60 s. Over the first few minutes of the reaction  $[\text{CH}_3\text{OH}]$  and  $[\text{CH}_2\text{O}]$  increased linearly in time, showing that the removal of  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$  by secondary reactions is negligible. Figure S5 (Supporting Information) shows that at later reaction times  $[\text{CH}_3\text{OH}]$  vs time and  $[\text{CH}_2\text{O}]$  vs time curve down due to the secondary reactions of the products, predominantly the  $\text{CH}_3\text{OH} + \text{Cl}$  and  $\text{CH}_2\text{O} + \text{Cl}$  reactions. Numerical simulations carried out using a chemical mechanism described in the Supporting Information for the reaction system at 298 K show that, following about 25 s induction time,  $[\text{CH}_3\text{OH}]$  and  $[\text{CH}_2\text{O}]$  increase linearly during the first few minutes of the reaction (Figure S6).

Using the integrating rate ratio for the two parallel reactions R4.a and R4.b, eq 6 is obtained.

$$\frac{[\text{CH}_2\text{O}]_b}{[\text{CH}_3\text{OH}]} = \frac{2k_{4,b}}{k_{4,a}} \quad (6)$$

Here  $[\text{CH}_2\text{O}]_b$  is the concentration of  $\text{CH}_2\text{O}$  formed by reaction R4.b followed by reaction R2. Taking into account that FTIR measures the sum of the concentrations of  $\text{CH}_2\text{O}$  produced by the two channels, i.e.,  $[\text{CH}_2\text{O}]_a$  produced by reaction R4.a and  $[\text{CH}_2\text{O}]_b$  obtained by reactions R4.b + R2, and  $[\text{CH}_2\text{O}]_a = [\text{CH}_3\text{OH}]$ , eq 7 is derived from eq 6. Equation 7 was employed in previous FTIR product studies of the  $\text{CH}_3\text{O}_2$  self-reaction.<sup>15,19</sup>

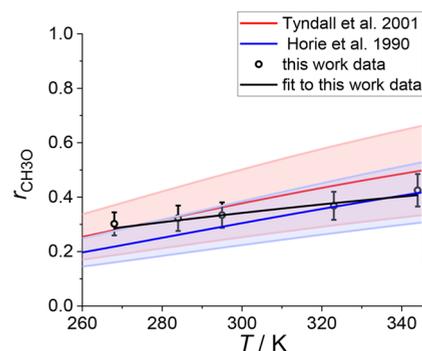
$$\frac{[\text{CH}_2\text{O}]_{\text{overall}}}{[\text{CH}_3\text{OH}]} = \frac{[\text{CH}_2\text{O}]_a + [\text{CH}_2\text{O}]_b}{[\text{CH}_3\text{OH}]} = \frac{k_{4,a} + 2k_{4,b}}{k_{4,a}} \quad (7)$$

Using eq 7 the branching ratio of the reaction channel R4.b, which produces  $\text{CH}_3\text{O}$ , is given by

$$r_{\text{CH}_3\text{O}} = \frac{k_{4,b}}{k_{4,a} + k_{4,b}} = \frac{[\text{CH}_2\text{O}]_{\text{overall}} - [\text{CH}_3\text{OH}]}{[\text{CH}_2\text{O}]_{\text{overall}} + [\text{CH}_3\text{OH}]} \quad (8)$$

The branching ratio  $r_{\text{CH}_3\text{O}}$  was determined using  $[\text{CH}_2\text{O}]_{\text{overall}}$  and  $[\text{CH}_3\text{OH}]$  measured at early reaction times, when the product concentrations increased linearly in time (Figure S5 in the Supporting Information). A number (6–20) of values of  $r_{\text{CH}_3\text{O}}$  were obtained at each temperature, 268, 284, 295, 323, and 344 K. Figure S7 (Supporting Information) shows that there was no trend with time in the extracted values over the initial few minutes used to determine  $r_{\text{CH}_3\text{O}}$ , and thus the secondary reactions of  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OH}$  can be neglected in the analysis.

The mean values of  $r_{\text{CH}_3\text{O}}$  are shown in Figure 1 and Table S2 (Supporting Information). The results show a positive temperature dependence which can be characterized by  $r_{\text{CH}_3\text{O}} = 1/\{1 + [\exp(600 \pm 85)/T]/(3.9 \pm 1.1)\}$ , i.e.,  $k_{4,b}/k_{4,a} = (3.9 \pm 1.1) \times \exp(-600 \pm 85)/T$ . There have been two temperature dependence studies of the branching ratios



**Figure 1.** Product branching ratio for the channel giving  $\text{CH}_3\text{O}$  of the  $\text{CH}_3\text{O}_2$  self-reaction,  $r_{\text{CH}_3\text{O}}$ , as a function of temperature,  $T$ . The data obtained in this work are shown as open circles with the fit result,  $1/\{1 + [\exp(600 \pm 85)/T]/(3.9 \pm 1.1)\}$ , shown in black. The blue line and shading show the result of Horie et al.,<sup>20</sup>  $r_{\text{CH}_3\text{O}} = 1/\{1 + [\exp(1131 \pm 30/T)]/(19 \pm 5)\}$  and the red line and shading show  $r_{\text{CH}_3\text{O}}$  vs  $T$  derived from  $k_{4,b}/k_{4,a}$  vs  $T$  evaluated by Tyndall et al.,<sup>21</sup>  $(26.2 \pm 6.6) \times \exp[-(1130 \pm 240)/T]$  and recommended by the Jet Propulsion Laboratory evaluation.<sup>6</sup> All the errors are given at the  $2\sigma$  level.

previously, in the range 388–573 K<sup>7</sup> and between 223–333 K.<sup>20</sup> The result obtained by Horie et al.,<sup>20</sup>  $r_{\text{CH}_3\text{O}} = 1/\{1 + [\exp(1131 \pm 30/T)]/(19 \pm 5)\}$ , is shown in Figure 1, as the temperature range used by these authors overlaps with the range of temperatures where the measurements reported in the present work were carried out. In addition, Figure 1 shows  $r_{\text{CH}_3\text{O}}$  derived from the evaluation of Tyndall et al.,<sup>21</sup>  $k_{4,b}/k_{4,a} = (26.2 \pm 6.6) \times \exp[-(1130 \pm 240)/T]$ , which is recommended by the Jet Propulsion Laboratory (JPL) evaluation.<sup>6</sup>

The values found by this work have overlapping error limits with the results reported by Horie et al.<sup>20</sup> and the values given by the recommendation of Tyndall et al.<sup>21</sup> at the  $2\sigma$  level. However, the temperature dependence measured by Horie et al.<sup>20</sup> and the temperature dependence recommended by Tyndall et al.<sup>21</sup> are steeper than the increase in the value of  $r_{\text{CH}_3\text{O}}$  with the temperature found in this study. The result at 295 K,  $r_{\text{CH}_3\text{O}}(\text{this work}) = 0.34 \pm 0.05$ , is between the result of Horie et al.,<sup>20</sup>  $r_{\text{CH}_3\text{O}}(\text{Horie et al.}) = 0.29 \pm 0.08$ , and the value recommended by Tyndall et al.,<sup>21</sup>  $r_{\text{CH}_3\text{O}}(\text{Tyndall et al.}) = 0.36 \pm 0.12$  (uncertainties at  $2\sigma$  level).

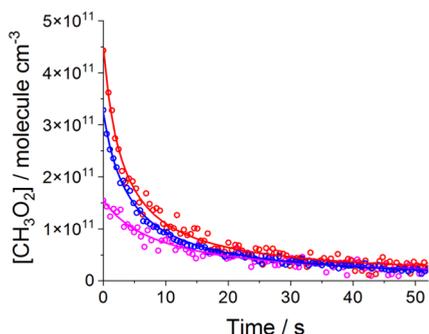
The evaluation of Tyndall et al.<sup>21</sup> is based on the results of Horie et al.<sup>20</sup> between 223–333 K, Lightfoot et al.<sup>7</sup> in the range 388–573 K, results published prior to 1990 at  $T \geq 373$  K, and the result of the evaluation of the room temperature values,  $r_{\text{CH}_3\text{O}}(298 \text{ K}) = 0.37 \pm 0.06$ .<sup>15</sup> The study of Horie et al.<sup>20</sup> is the single experimental study performed at temperatures in a range around room temperature, i.e., (293<sup>+40</sup><sub>-70</sub>) K. The results of the present study agree well with the values reported by Horie et al.<sup>20</sup> at 323 and 344 K (Figure 1). However, going down in temperature  $r_{\text{CH}_3\text{O}}(\text{this work})$  is increasingly higher than  $r_{\text{CH}_3\text{O}}(\text{Horie et al.})$ .<sup>20</sup>

Horie et al.<sup>20</sup> carried out flow tube experiments using photolysis of  $\text{CH}_4/\text{Cl}_2/\text{O}_2$  mixtures to measure the ratio  $[\text{CH}_2\text{O}]/[\text{CH}_3\text{OH}]$ , where  $\text{CH}_2\text{O}$  and  $\text{CH}_3\text{OH}$  were produced by the  $\text{CH}_3\text{O}_2$  self-reaction, employing matrix isolation Fourier transform infrared spectroscopy. The authors performed numerical simulations based on a complex model to vary the rate coefficients of the self-reaction channels to match the measured values for  $[\text{CH}_2\text{O}]/[\text{CH}_3\text{OH}]$ . The authors

found no evidence for the formation of  $\text{CH}_3\text{OOCH}_3$  by the reaction channel R4.c. However, two sets of numerical simulations were performed: assuming a branching ratio of 0.1 for reaction R4.c and excluding reaction R4.c from the chemical mechanism used in the numerical simulations. Figure 1 shows the reported temperature dependence derived averaging the results generated by the two sets of simulations.<sup>20</sup> Considering a zero contribution for reaction R4.c, in line with the present recommendations,<sup>5,6</sup> the reported values of  $r_{\text{CH}_3\text{O}}$  (Horie et al.) increase by 5% over the temperature range 268–344 K and are lower than  $r_{\text{CH}_3\text{O}}$  (this work) by 7% at 295 K, 14% at 284 K, and 22% at 268 K.

The present work measured  $[\text{CH}_2\text{O}]$  and  $[\text{CH}_3\text{OH}]$  *in situ* to determine  $r_{\text{CH}_3\text{O}}$  (eq 8), while Horie et al.<sup>20</sup> trapped the reaction products outside the reaction cell in a  $\text{CO}_2$  matrix at 50 K to analyze them by IR spectroscopy to obtain  $[\text{CH}_2\text{O}]/[\text{CH}_3\text{OH}]$ , which was then used in the determination of  $r_{\text{CH}_3\text{O}}$ . The concentrations of  $\text{CH}_2\text{O}$  produced by the self-reaction were corrected taking into account  $\text{CH}_2\text{O}$  formed in the matrix using a correction factor less than 10%. The lower values obtained for  $r_{\text{CH}_3\text{O}}$  (Horie et al.) relative to  $r_{\text{CH}_3\text{O}}$  (this work) at  $T \leq 295$  K can be explained by a process leading to the  $\text{CH}_2\text{O}$  removal enhanced by reducing the reaction temperature which was not included in the reaction mechanism employed in the analysis performed by the authors.<sup>20</sup> Horie et al.<sup>20</sup> reported evidence of aerosol formation at 213 K resulting in unaccounted removal of  $\text{CH}_2\text{O}$  leading to a value of  $[\text{CH}_2\text{O}]/[\text{CH}_3\text{OH}]$  lower than unity, a result which was not expected based on the reaction mechanism; the results obtained at 213 K were thus excluded from the analysis. The experiments below room temperature used in the determination of  $r_{\text{CH}_3\text{O}}$ —i.e., in the range 223–298 K—were reported “free” of aerosols. However,  $[\text{CH}_2\text{O}]$  and  $[\text{CH}_3\text{OH}]$  in the experiments were relatively large, a few times higher than in the present work, increasing the potential of oligomers/particle formation at low temperatures.

**Kinetics of the  $\text{CH}_3\text{O}_2$  Self-Reaction.** Figure 2 shows examples of  $\text{CH}_3\text{O}_2$  decay generated by turning the HIRAC lamps off following the production of  $\text{CH}_3\text{O}_2$  by the Cl atom initiated oxidation of  $\text{CH}_4$  in the presence of  $\text{O}_2$  (reactions R6 and R7) at 323 K. Kinetic decays were obtained in a similar fashion at all temperatures. The  $\text{CH}_3\text{O}_2$  decays at each



**Figure 2.** Examples of observations of  $\text{CH}_3\text{O}_2$  (open circles) and fits to the data (solid lines) generated employing eq 9. The experiments used  $\text{Cl}_2/\text{CH}_4/\text{O}_2$  and black lamps (see main text for details); 323 K and 1000 mbar mixture of  $\text{N}_2:\text{O}_2 = 4:1$ . At time zero the lamps were turned off.  $[\text{CH}_4]_0 = 2.5 \times 10^{17}$  molecules  $\text{cm}^{-3}$  for all the kinetic decays. Initial  $\text{Cl}_2$  concentrations:  $3.3 \times 10^{14}$  molecules  $\text{cm}^{-3}$  (red),  $2.4 \times 10^{14}$  molecules  $\text{cm}^{-3}$  (blue), and  $7.5 \times 10^{13}$  molecules  $\text{cm}^{-3}$  (magenta).

temperature, 268, 284, 295, 323, and 344 K, measured using FAGE were fitted simultaneously to the integrated second-order rate law equation describing the  $\text{CH}_3\text{O}_2$  self-reaction (R4):

$$\frac{1}{[\text{CH}_3\text{O}_2]_t} = \frac{1}{[\text{CH}_3\text{O}_2]_0} + 2k_{\text{obs}}t \quad (9)$$

where  $[\text{CH}_3\text{O}_2]_t$  is the methyl peroxy concentration at reaction time  $t$ ,  $[\text{CH}_3\text{O}_2]_0$  is the initial concentration when the lights are switched off and  $k_{\text{obs}}$  is the observed rate coefficient. In line with previous analysis,<sup>23</sup> this work found that the loss of  $\text{CH}_3\text{O}_2$  to the walls of HIRAC was negligible over the time scale of 0.5–1 min of the kinetic measurements at all temperatures employed, and hence a wall loss was not included in the kinetic analysis. Typically about 20  $\text{CH}_3\text{O}_2$  decays were fitted simultaneously at each temperature to obtain  $k_{\text{obs}}$  with the results shown in Table 1.

**Table 1.** Observed Rate Coefficient,  $k_{\text{obs}}$  for the  $\text{CH}_3\text{O}_2$  Self-Reaction Measured in This Work

Temperature/K	$k_{\text{obs}}$ (this work) <sup>a</sup> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
268	$(3.2 \pm 1.1) \times 10^{-13}$
284	$(2.9 \pm 1.0) \times 10^{-13}$
295	$(2.7 \pm 0.9) \times 10^{-13}$
323	$(3.4 \pm 1.4) \times 10^{-13}$
344	$(2.6 \pm 0.9) \times 10^{-13}$

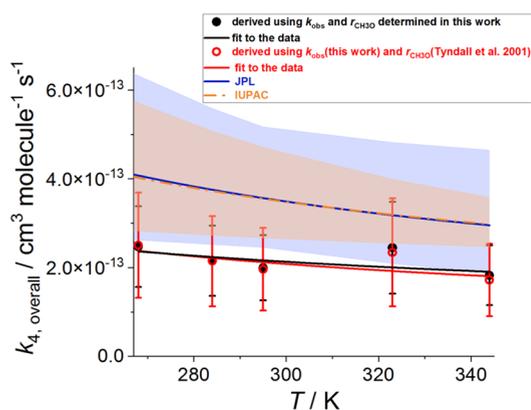
<sup>a</sup>errors are  $2\sigma$ .

The observed rate coefficient is larger than the second-order rate coefficient of just the  $\text{CH}_3\text{O}_2$  recombination reaction (R4),  $k_4$ , as the methoxy radicals generated by channel R4.b react rapidly with molecular oxygen, which is present in large excess,  $5 \times 10^{18}$  molecules  $\text{cm}^{-3}$ , to produce  $\text{HO}_2$  (reaction R2), which in turn reacts with another  $\text{CH}_3\text{O}_2$  radical (reaction R5). As each  $\text{HO}_2$  radical consumes one  $\text{CH}_3\text{O}_2$  species (reaction R5) on the time scale of reaction R4,  $k_4$  is derived from  $k_{\text{obs}}$  as follows:<sup>7,11</sup>

$$k_{\text{obs}} = k_4(1 + r_{\text{CH}_3\text{O}}) \quad (1)$$

where  $r_{\text{CH}_3\text{O}}$  is the branching ratio for the reaction channel R4.b. The applicability of eq 1 in the analysis of the kinetic data generated by the HIRAC experiments was demonstrated by modeling the observed temporal decays using a variety of  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  concentrations representative for the HIRAC experiments and incorporating a heterogeneous loss of  $\text{HO}_2$  in the model relevant for the experiments:<sup>22,23</sup>  $k_{\text{loss}} = 0.01\text{--}0.1$  s<sup>-1</sup>. The results showed that the removal of  $\text{HO}_2$  by wall loss is negligible and thus can be excluded from the model.<sup>22</sup>

Figure 3 shows the determined temperature dependence for  $k_4$ . At all temperatures employed, the values of  $k_4$  obtained using both  $k_{\text{obs}}$  and  $r_{\text{CH}_3\text{O}}$  determined in this work are practically the same as the  $k_4$  values obtained using  $k_{\text{obs}}$  determined in this work and  $r_{\text{CH}_3\text{O}}$  given by the evaluation of Tyndall et al.,<sup>21</sup> which is recommended by JPL.<sup>6</sup> Using the value of  $r_{\text{CH}_3\text{O}} = 0.34 \pm 0.05$  determined at 295 K in this work the rate coefficient of the overall reaction  $k_4(295 \text{ K}) = (2.0 \pm 0.7) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (uncertainties at  $2\sigma$  level). Using the value of  $r_{\text{CH}_3\text{O}}(295 \text{ K}) = 0.36 \pm 0.12$  recommended by Tyndall et al.<sup>21</sup> does not change the result at this level of precision:  $k_4(295 \text{ K}) = (2.0 \pm 0.9) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (uncertainties quoted at  $2\sigma$  level). The negative temperature



**Figure 3.** Temperature dependence of the overall rate coefficient of the  $\text{CH}_3\text{O}_2$  self-reaction (R4),  $k_4$ . The data generated using  $k_{\text{obs}}$  and  $r_{\text{CH}_3\text{O}_2}$  obtained in this work (black circles) are plotted with the data generated using  $k_{\text{obs}}$  measured by this work and  $r_{\text{CH}_3\text{O}_2}$  given by the evaluation of Tyndall et al.<sup>21</sup> (open red circles) and  $k_4$  recommended by JPL (blue line and shading)<sup>6</sup> and IUPAC (orange dashed line and shading).<sup>5</sup> The blue and orange shadings show the  $2\sigma$  uncertainties in the JPL and IUPAC recommendations. The results of the fit to the data are  $k_4 = (9.1 \pm 5.3) \times 10^{-14} \times \exp((252 \pm 174)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (black line) and  $k_4 = (6.8 \pm 4.1) \times 10^{-14} \times \exp((335 \pm 179)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (red line). The parametrization of the temperature dependence of  $k_4$  recommended by JPL and IUPAC are  $k_4(\text{JPL}) = 9.5 \times 10^{-14} \times \exp(390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>16</sup> and  $k_4(\text{IUPAC}) = 1.03 \times 10^{-13} \times \exp((365)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup>

dependence obtained employing  $r_{\text{CH}_3\text{O}_2}$  determined in this work can be characterized by  $k_4 = (9.1 \pm 5.3) \times 10^{-14} \times \exp((252 \pm 174)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Figure 3 compares the result of this work with  $k_4$  vs  $T$  recommended by JPL and IUPAC. The JPL and IUPAC recommendations are similar to each other:  $k_4(\text{JPL}) = 9.5 \times 10^{-14} \times \exp(390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>16</sup> and  $k_4(\text{IUPAC}) = 1.03 \times 10^{-13} \times \exp((365 \pm 200)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5</sup> On average, the results of this work are  $\sim 40\%$  lower than the values calculated using the JPL and IUPAC recommendations. However, the results of this work have overlapping error limits at the  $2\sigma$  level with both recommendations.

The previous studies upon which the JPL<sup>6</sup> and IUPAC<sup>5</sup> recommendations are based utilized the UV-absorption of  $\text{CH}_3\text{O}_2$  at fixed wavelengths in the range  $\sim 210$ – $270$  nm (typically 250 nm) usually to determine the ratio between the observed rate coefficient and the absorption cross-section of  $\text{CH}_3\text{O}_2$ ,  $k_{\text{obs}}/\sigma_{\text{CH}_3\text{O}_2}$ .<sup>5,6</sup> The values used for  $\sigma_{\text{CH}_3\text{O}_2}$  by the previous UV-absorption studies vary significantly, between  $(2.5$ – $4.8) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$  at 250 nm, leading to a large variation in  $k_{\text{obs}}$  across the studies, which at 298 K ranges between  $k_{\text{obs}} = (3.0$ – $5.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>7–14</sup> The 2020 JPL<sup>6</sup> evaluation report recommends the cross sections obtained by the re-evaluation of Tyndall et al. in 2001<sup>21</sup> of the previous reported UV-absorption spectra. At 250 nm Tyndall et al.<sup>21</sup> recommend  $\sigma_{\text{CH}_3\text{O}_2(250 \text{ nm})} = 3.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . Our calculations show that using  $\sigma_{\text{CH}_3\text{O}_2}$  reported by Tyndall et al.<sup>21</sup> and the ratios  $k_{\text{obs}}/\sigma_{\text{CH}_3\text{O}_2}$  found in the previous kinetic studies,<sup>7–11,13,14</sup> the range of the values of  $k_{\text{obs}}$  at 298 K is reduced to  $(4.1$ – $5.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The present result at 298 K,  $k_{\text{obs}} = 2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , is 30% smaller than the lowest value of  $4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and 40% lower than the JPL<sup>6</sup> and IUPAC<sup>5</sup> recommendations of  $k_{\text{obs}} = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

There is a significant difference between the results obtained here and the recommendations,<sup>5,6</sup> and here we explore possible reasons for this discrepancy. The previous studies used either the flash photolysis (FP) technique<sup>7–11</sup> or the molecular modulation (MM) method<sup>12–14</sup> to generate  $\text{CH}_3\text{O}_2$  radicals employing photolytic mixtures of  $\text{CH}_4/\text{Cl}_2/\text{O}_2$ . The discrepancy between  $k_{\text{obs}}$  determined in here and the results reported in the FP studies<sup>7–11</sup> could be due to unaccounted secondary chemistry of  $\text{CH}_3\text{O}_2$  due to the high radical concentrations, on the order of  $[\text{CH}_3\text{O}_2]$  of  $10^{13}$ – $10^{14} \text{ molecules cm}^{-3}$ , and/or unaccounted spectral interferences. The MM experiments<sup>12–14</sup> used 1–2 orders of magnitude lower concentrations of  $\text{CH}_3\text{O}_2$  than  $[\text{CH}_3\text{O}_2]$  in the FP studies,<sup>7–11</sup> i.e., concentrations on the order  $10^{12} \text{ molecules cm}^{-3}$ , to minimize the impact of the secondary chemistry on  $k_{\text{obs}}$ . However, as this method consisted of modulating the photolysis and hence the production of radicals by alternating the time with the lamps switched on and the time with the lamps turned off, a potential important source of error was the buildup of products absorbing in the UV range of the measurements (see below). The contributions of the absorbing products (see below) were subtracted from the overall absorbance measured by the MM experiments<sup>12,14</sup> to extract the absorbance of  $\text{CH}_3\text{O}_2$ , and thus the extracted absorbance depended on the concentrations and the cross sections attributed to the products. Note that the LIF method is selective and more sensitive, with a limit of detection for  $\text{CH}_3\text{O}_2$  of  $2.0 \times 10^9 \text{ molecules cm}^{-3}$  for a signal-to-noise ratio of 2, 1 s averaging time of the online data points measured during the kinetic decay, and 60 s averaging period for the offline data points recorded at the end of the experiment. Therefore, the LIF method requires significantly lower radical concentrations than the FP and MM studies; here,  $[\text{CH}_3\text{O}_2]_0 = (0.1$ – $1) \times 10^{12} \text{ molecules cm}^{-3}$ , which helps to minimize potential secondary chemistry.

The FP studies<sup>7–11</sup> typically derived the  $k_{\text{obs}}/\sigma_{\text{CH}_3\text{O}_2}$  ratio fitting either eq 10 or eq 11 to the measured optical absorbance ( $A_t$ ) or absorption coefficient ( $\alpha_t$ ) at/around 250 nm.

$$\frac{1}{A_t} = \frac{1}{A_0} + 2 \frac{k_{\text{obs}}}{\sigma_{\text{CH}_3\text{O}_2} l} t \quad (10)$$

$$\frac{1}{\alpha_t} = \frac{1}{\alpha_0} + 2 \frac{k_{\text{obs}}}{\sigma_{\text{CH}_3\text{O}_2}} t \quad (11)$$

Here  $A_0$  and  $\alpha_0$  are the absorbance and the absorption coefficient at the time zero of the reaction, respectively, and  $l$  is the total optical path length.

To investigate the potential impact of the secondary chemistry on the  $\text{CH}_3\text{O}_2$  kinetic decays in the FP studies<sup>7–11</sup> numerical simulations were performed using a reaction system at 298 K described in the Supporting Information (Table S1). The previous kinetic studies of the  $\text{CH}_3\text{O}_2$  recombination reaction<sup>7–14</sup> did not investigate the impact of the  $\text{CH}_3\text{O}_2$  reaction with the ClO radicals produced by the  $\text{CH}_3\text{O}_2 + \text{Cl}$  reaction on the  $\text{CH}_3\text{O}_2$  kinetic decay. The kinetics of the  $\text{CH}_3\text{O}_2 + \text{Cl}$  reaction<sup>34,35</sup> was studied in the years around 1995 and thus after all the previous kinetic studies of the  $\text{CH}_3\text{O}_2$  self-reaction (1980–1990).<sup>5,6</sup> The  $\text{CH}_3\text{O}_2 + \text{Cl}$  reaction is fast producing ClO (rate coefficient of  $7.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K).<sup>34</sup> The generated ClO radicals predominantly react with  $\text{CH}_3\text{O}_2$  with an overall rate coefficient of  $2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.<sup>6</sup>

The simulations used  $k_4 = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as determined in this work and  $r_{\text{CH}_3\text{O}_2} = 0.37$ .<sup>5,6</sup> The Supporting Information shows examples of the results of the numerical simulations using concentrations representative for the FP studies:<sup>7–11</sup>  $[\text{CH}_4]_0 = 5 \times 10^{17} \text{ molecules cm}^{-3}$  and  $[\text{Cl}]_0 = 1.4 \times 10^{14} \text{ molecules cm}^{-3}$ . As the  $\text{Cl} + \text{CH}_4$  reaction is relatively slow (rate coefficient =  $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K)<sup>36</sup> about 7% of the Cl atoms react with  $\text{CH}_3\text{O}_2$  to produce ClO. Subsequently ClO predominantly reacts with  $\text{CH}_3\text{O}_2$  (peak  $[\text{CH}_3\text{O}_2] = 1.0 \times 10^{14} \text{ molecules cm}^{-3}$  as shown in the Supporting Information). Therefore, fitting eq 8 to the  $\text{CH}_3\text{O}_2$  temporal decay simulated using the mechanism which includes the secondary chemistry results in  $k_{\text{obs}}(\text{fit}) = (3.8 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Using eq 9,  $k_4(\text{fit}) = 2.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is obtained, which is 33% higher than the value of  $k_4$  determined from this work and used as an input in the numerical simulations,  $k_4(\text{simulations}) = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . To investigate the sensitivity of the results to the presence of the  $\text{CH}_3\text{O}_2 + \text{ClO}$  reaction in the chemical mechanism used, the simulations with  $[\text{CH}_4]_0 = 5 \times 10^{17} \text{ molecules cm}^{-3}$  and  $[\text{Cl}]_0 = 1.4 \times 10^{14} \text{ molecules cm}^{-3}$  were repeated, but this time in the absence of the  $\text{CH}_3\text{O}_2 + \text{ClO}$  reaction. Without the  $\text{CH}_3\text{O}_2 + \text{ClO}$  reaction,  $k_{\text{obs}}(\text{fit}) = (3.0 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  resulting in  $k_4(\text{fit}) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  being obtained, which is almost the same with the value used as input in the simulations,  $k_4(\text{simulations}) = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Hence, for  $[\text{CH}_4]_0 = 5 \times 10^{17} \text{ molecules cm}^{-3}$  and  $[\text{Cl}]_0 = 1.4 \times 10^{14} \text{ molecules cm}^{-3}$ , the values of  $k_{\text{obs}}$  and  $k_4$  obtained from the fit to the simulated  $\text{CH}_3\text{O}_2$  decay are considerably larger if the secondary chemistry is included to generate the decay. As the studies using the flash photolysis technique<sup>7–11</sup> typically employed  $\sim[\text{CH}_4]_0 = 10^{17} \text{ molecules cm}^{-3}$  and  $\sim[\text{Cl}]_0 = 10^{14} \text{ molecules cm}^{-3}$  the studies significantly overestimated  $k_{\text{obs}}$  and thus  $k_4$ .

In the present study the concentrations of  $[\text{CH}_3\text{O}_2]$ ,  $[\text{Cl}]$ , and  $[\text{ClO}]$  were in a steady-state with the lamps turned on, and the  $\text{CH}_3\text{O}_2$  decays were generated by switching the lamps off. Numerical simulations were performed over 5 min to mimic the chemistry with the lamps turned on using  $[\text{CH}_4]_0 = 3.0 \times 10^{17} \text{ molecules cm}^{-3}$  with  $[\text{Cl}_2]_0 = 3.0 \times 10^{14} \text{ molecules cm}^{-3}$  representative for the present study and adding the  $\text{Cl}_2$  photolysis to the chemistry mechanism including the  $\text{CH}_3\text{O}_2 + \text{Cl}$  and  $\text{CH}_3\text{O}_2 + \text{ClO}$  reactions (Supporting Information). After 5 min with the lamps on,  $[\text{CH}_3\text{O}_2] = 5 \times 10^{11} \text{ molecules cm}^{-3}$ ,  $[\text{Cl}] = 7.0 \times 10^6 \text{ molecules cm}^{-3}$ , and  $[\text{ClO}] = 2.4 \times 10^8 \text{ molecules cm}^{-3}$ . The concentrations of all the species in the chemistry mechanism obtained after 5 min were input into numerical simulations using the same chemistry mechanism except without  $\text{Cl}_2$  photolysis to mimic the chemistry during the time with the lamps turned off. Virtually all Cl atoms and ClO radicals were removed on a time scale of hundreds of microseconds and seconds, respectively. As  $[\text{Cl}]_0 = 7.0 \times 10^6 \text{ molecules cm}^{-3}$  and  $[\text{ClO}]_0 = 2.4 \times 10^8 \text{ molecules cm}^{-3}$ , and hence orders of magnitude lower than  $[\text{Cl}]_0 = 1.4 \times 10^{14} \text{ molecules cm}^{-3}$  and a peak of  $[\text{ClO}] = 1.0 \times 10^{13} \text{ molecules cm}^{-3}$  in the simulations using concentrations representative for the FP studies,<sup>7–11</sup> the simulated  $\text{CH}_3\text{O}_2$  decays were not impacted by the chlorine species secondary chemistry (Figure S3). The fit of eq 9 to the  $\text{CH}_3\text{O}_2$  decay provided a value of  $k_{\text{obs}}(\text{fit}) = (3.0 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, which results in  $k_4(\text{fit}) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , i.e., practically the same as the value measured by the present

experiments  $k_4 = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Therefore, no impact by the secondary chemistry of  $\text{CH}_3\text{O}_2$  included in the simulations (Supporting Information) on the value determined for  $k_4$  was found in the present study. Hence in the absence of secondary chemistry the value of  $k_4$ , as determined in this work, is considerably lower than  $k_4$  when the secondary chemistry is present as a result of much higher initial  $[\text{Cl}]$  concentrations.

We now consider potential spectral interferences in previous work which monitored  $\text{CH}_3\text{O}_2$  concentrations using UV absorption. At the typical  $\lambda = 250 \text{ nm}$  used to monitor the  $\text{CH}_3\text{O}_2$  absorption by the FP studies,<sup>7–11</sup> the cross-section of ClO,  $\sigma_{\text{ClO}} = 3.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ <sup>16</sup> and the cross-section of  $\text{CH}_3\text{O}_2$ ,  $\sigma_{\text{CH}_3\text{O}_2} = 3.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ <sup>21</sup> are similar, and hence numerical simulations were used to investigate the impact of any ClO spectral interference on the results of the FP studies. The concentrations of the species generated by numerical simulations using the representative concentrations for the FP studies of  $[\text{CH}_4]_0 = 5 \times 10^{17} \text{ molecules cm}^{-3}$  and  $[\text{Cl}]_0 = 1.4 \times 10^{14} \text{ molecules cm}^{-3}$  in the model that includes the  $\text{CH}_3\text{O}_2 + \text{ClO}$  reaction were multiplied with their respective cross sections<sup>6,21</sup> to obtain the absorption coefficients of  $\text{CH}_3\text{O}_2$  and ClO:

$$\alpha_{i,t} = \sigma_i [i]_t \quad (12)$$

where  $\alpha_{i,t}$  is the absorption coefficient of species  $i$  ( $\text{CH}_3\text{O}_2$  or ClO) at reaction time  $t$ ,  $\sigma_i$  is the absorption cross-section of species  $i$  at 250 nm and  $[i]_t$  is the concentration of species  $i$  at time  $t$ . Figure S4 in the Supporting Information shows the generated  $\alpha_{\text{CH}_3\text{O}_2,t}$  and  $\alpha_{\text{ClO},t}$  and their sum,  $\Sigma\alpha_{i,t} = \alpha_{\text{CH}_3\text{O}_2,t} + \alpha_{\text{ClO},t}$ . The results (Figure S4) show that there is a minor contribution of  $\alpha_{\text{ClO},t}$  to  $\Sigma\alpha_{i,t}$  at the start of the reaction, i.e.,  $\sim 8\%$  in the first millisecond of the reaction, which drops to 3% at  $t = 10 \text{ ms}$ . The fit of the eq 11 (see above) to  $\Sigma\alpha_{i,t}$  vs time resulted in  $k_{\text{obs}}/\sigma_{\text{CH}_3\text{O}_2}$ . Using  $\sigma_{\text{CH}_3\text{O}_2} = 3.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ <sup>21</sup> a value of  $k_{\text{obs}} = (3.9 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is obtained, which is 3% higher than  $k_{\text{obs}}$  given fitting eq 9 to the temporal decay of  $[\text{CH}_3\text{O}_2]$  generated by the same numerical simulations (Figure S1). The result suggests that there was no significant optical interference due to the ClO absorption which impacted the previous determinations of  $k_{\text{obs}}$  using the FP technique.<sup>7–11</sup>

The molecular modulation (MM) studies<sup>12–14</sup> used the time-resolved modulated UV-absorption (absorption waveform) generated in the range 210–270 nm via switching the photolysis lamps on and off with a typical frequency of  $10^{-1} \text{ Hz}$  (order of magnitude) to determine  $k_{\text{obs}}$  and  $\sigma_{\text{CH}_3\text{O}_2}$ . The absorption waveform consisted of an initial rise followed by a pseudo-steady-state and then a decay during the dark phase of the modulation period.<sup>12–14</sup> The modulated absorption components depended on a relatively large number of parameters: illumination time, rate of  $\text{Cl}_2$  photolysis, kinetic parameters, and absorbing species cross sections.<sup>12–14</sup> Photolytic mixtures of  $\text{CH}_4/\text{Cl}_2/\text{O}_2$  were flowed through the reactor to minimize the buildup of the products. However, the residence times of the gases in the reaction cell were relatively long, for example, 35 and 60 s.<sup>13,14</sup> The contributions of the absorbing products accumulating over the photolysis cycles was calculated and subtracted from the observed absorption to derive the modulated absorption of  $\text{CH}_3\text{O}_2$ .<sup>12,14</sup> The contribution of the products were important in the range 210–250 nm where the cross sections of  $\text{HO}_2$  (formed by reaction R2 and the reactions of Cl with the products  $\text{CH}_3\text{OH}$

and  $\text{CH}_2\text{O}$ ) and  $\text{CH}_3\text{OOH}$  (produced by the  $\text{CH}_3\text{O}_2 + \text{HO}_2$  reaction) increases rapidly with decreasing  $\lambda$ .<sup>6</sup> However, the cross sections of  $\text{HO}_2$  and/or  $\text{CH}_3\text{OOH}$  were significantly overestimated in the MM studies.<sup>12–14</sup> The references cited for the cross-section of  $\text{HO}_2$  by Cox and Tyndall<sup>12</sup> reported  $\sigma_{\text{HO}_2}$  larger than the JPL recommendations<sup>6</sup> by 60–70% in the range 210–250 nm<sup>37</sup> and by ~10% between 210–220 nm.<sup>38</sup> The cross-section of  $\text{HO}_2$ <sup>39</sup> used by Simon et al.<sup>14</sup> is ~30% larger than the JPL recommendation<sup>6</sup> between 210–240 nm and by ~60% at 250 nm. Both the studies of Cox and Tyndall<sup>12</sup> and Jenkin et al.<sup>13</sup> employed values for  $\sigma_{\text{CH}_3\text{OOH}}$  at least 40–50% higher than the JPL recommendation in the range 210–250 nm.<sup>6</sup> An overestimation of the contributions of these species to the measured absorbance results in an underestimation of the  $\text{CH}_3\text{O}_2$  absorbance,  $A_{\text{CH}_3\text{O}_2}$ , which in turn results in an overestimation of  $k_{\text{obs}}/\sigma_{\text{CH}_3\text{O}_2}$  (eq 10).

In addition, the  $\text{CH}_3\text{O}_2$  loss to the walls of the reaction cell were not accounted for by neither the FP studies<sup>7–11</sup> nor the MM studies<sup>12–14</sup> and could also result in an overestimation of  $k_{\text{obs}}$ . As the  $\text{CH}_3\text{O}_2$  self-reaction is slow, the wall-loss could significantly contribute to the overall  $\text{CH}_3\text{O}_2$  removal in the previous studies.

## DISCUSSION OF THE FAGE INSTRUMENT CALIBRATION

As LIF is not an absolute detection method, the FAGE instrument required calibration and a calibration factor,  $C_{\text{CH}_3\text{O}_2}$ , is used to convert the measured signal,  $S_{\text{CH}_3\text{O}_2}$ , to the  $\text{CH}_3\text{O}_2$  concentration:

$$[\text{CH}_3\text{O}_2] = \frac{S_{\text{CH}_3\text{O}_2}}{C_{\text{CH}_3\text{O}_2}} \quad (5)$$

To calibrate FAGE,  $\text{CH}_3\text{O}_2$  radicals were generated in known concentrations employing the 184.9 nm photolysis of water vapor in synthetic air followed by the complete conversion of the generated OH radicals to  $\text{CH}_3\text{O}_2$  by reaction with  $\text{CH}_4$  in a large excess in the presence of  $\text{O}_2$ . Previous work described in detail the water vapor method of calibration and the uncertainties in the calibration factor,  $C_{\text{CH}_3\text{O}_2}$  (water vapor method).<sup>22</sup> As seen previously,<sup>22</sup> in this work an overall 34% error at  $2\sigma$  level was obtained for  $C_{\text{CH}_3\text{O}_2}$  (water vapor method) combining the systematic and statistical uncertainties. Similar overall errors, 31% and 36%, were reported for  $C_{\text{HO}_2}$  (water vapor method) previously.<sup>28,30</sup>

The photolysis of water vapor at 184.9 nm represents the most common method used to generate accurate concentrations of OH and  $\text{HO}_2$ . The method has been applied for many years for the calibration of FAGE instruments.<sup>24–26</sup> The reliability of the method has been confirmed by intercomparisons with alternative methods of calibration for OH and  $\text{HO}_2$ . The calibration of OH using the water vapor photolysis and the OH calibration based on the generation of OH by ozone reactions with alkenes have been found to agree within their experimental uncertainties.<sup>40</sup> Very good agreement (difference within 1–13%) has been obtained by comparing the OH measurements in the SAPHIR atmospheric simulation chamber using a number of FAGE instruments and instruments employing differential optical laser absorption spectroscopy (DOAS) and chemical ionization mass spectrometry (CIMS).<sup>41,42</sup> In the case of  $\text{HO}_2$ ,  $C_{\text{HO}_2}$  (water vapor method)

and the calibration factor obtained analyzing the kinetic decay of  $\text{HO}_2$  by its self-reaction generated in HIRAC,  $C_{\text{HO}_2}$  (kinetic method), were found in a very good agreement (difference within 8%).<sup>28,30</sup> However, a discrepancy within ~40% was found between  $C_{\text{CH}_3\text{O}_2}$  (water vapor method) and the  $\text{CH}_3\text{O}_2$  calibration factor determined using the kinetics of the second-order recombination of  $\text{CH}_3\text{O}_2$  observed in HIRAC and  $k_{\text{obs}}(298 \text{ K}) = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>5,6</sup>  $C_{\text{CH}_3\text{O}_2}$  (kinetic method).<sup>22,23</sup> As the error in the fraction of OH which is converted to  $\text{CH}_3\text{O}_2$  upon the addition of methane in the water vapor method is minor (4% at  $2\sigma$  level),<sup>22</sup> the discrepancy between the two calibration methods can be attributed to an overestimation of the reported value of  $k_{\text{obs}}$  for the  $\text{CH}_3\text{O}_2$  self-reaction at 298 K.<sup>5,6</sup> The ~40% difference in  $C_{\text{CH}_3\text{O}_2}$  (kinetic method) and  $C_{\text{CH}_3\text{O}_2}$  (water vapor method) resulted in different values for the gradient of the correlation plot of  $[\text{CH}_3\text{O}_2]$  measured by FAGE (y-axis) as a function of  $[\text{CH}_3\text{O}_2]$  measured by near-infrared cavity ring down spectroscopy, CRDS (x-axis), at 1000 mbar of synthetic air using the sensitivities from the two methods of calibration of FAGE:  $1.35 \pm 0.07$  (water vapor calibration) and  $0.92 \pm 0.05$  (kinetic method of calibration).<sup>23</sup> The results show a significantly better agreement with the kinetic method than with the water vapor method. A very good level of agreement between the FAGE and CRDS measurements of  $\text{CH}_3\text{O}_2$  was also obtained using the kinetic method for FAGE calibration at 100 mbar of synthetic air and 80 mbar of 3:1 He: $\text{O}_2$  mixture. The very good agreement achieved under all conditions when the kinetic method was employed for the FAGE calibration was expected as the kinetic method was also used to determine the absorption cross section of  $\text{CH}_3\text{O}_2$  from the temporal decays of the optical absorption coefficient of  $\text{CH}_3\text{O}_2$  and hence calibrate the CRDS method. Therefore, with both FAGE and CRDS calibrated using the same method, the intercomparison was not subject to any error in the rate coefficient,  $k_{\text{obs}}$  for the  $\text{CH}_3\text{O}_2$  self-reaction, and the obtained very good agreement provides a validation of the FAGE (water vapor) method to determine concentrations of  $\text{CH}_3\text{O}_2$ . The present result at 298 K,  $k_{\text{obs}} = 2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , shows a 40% reduction in the reported value of  $k_{\text{obs}} = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5,6</sup> A reduction of 40% in the reported  $k_{\text{obs}}$  would bring  $[\text{CH}_3\text{O}_2]_{\text{CRDS}}$  generated using the kinetic method of calibration into agreement with  $[\text{CH}_3\text{O}_2]_{\text{FAGE}}$  determined using the water vapor method.<sup>23</sup> Therefore, the FAGE–CRDS intercomparison also suggests that  $k_{\text{obs}} = 2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and thus  $k_4 = 2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, consistent with the values found in the present study.

## CONCLUSIONS

Experiments were carried out in the range 268–344 K and at 1000 mbar to measure  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$  generated by the  $\text{CH}_3\text{O}_2$  self-reaction in HIRAC using *in situ* FTIR detection to determine the product branching ratios in the self-reaction. The chemistry was initiated using photolysis of  $\text{Cl}_2/\text{CH}_4/\text{N}_2/\text{O}_2$  mixtures (photolysis range:  $\lambda = 350\text{--}400 \text{ nm}$ ). The temperature dependence of the product branching ratio of the reaction channel producing  $\text{CH}_3\text{O}$  can be described as  $r_{\text{CH}_3\text{O}} = 1/\{1 + [\exp(600 \pm 170)/T]/(3.9 \pm 2.2)\}$ . At 295 K  $r_{\text{CH}_3\text{O}}(\text{this work}) = 0.34 \pm 0.05$ , in agreement with the recommendations of JPL<sup>6</sup> and IUPAC:<sup>5</sup>  $r_{\text{CH}_3\text{O}}(\text{JPL}) = 0.36 \pm$

0.12 and  $r_{\text{CH}_3\text{O}(\text{IUPAC})} = 0.36 \pm 0.17$ . This is the second experimental study of the temperature dependence of the product branching ratios in a range including temperatures relevant for atmospheric chemistry. The positive temperature dependence found for  $r_{\text{CH}_3\text{O}}$  is less marked than the increase in  $r_{\text{CH}_3\text{O}}$  with temperature measured by the previous study performed in a temperature range around 298 K (223–333 K), which used matrix isolation FTIR.<sup>20</sup> The results of the present work for product branching agree well with the values obtained by Horie et al.<sup>20</sup> at 295, 323, and 344 K. By decreasing the temperature, the present results are increasingly higher than the results reported by Horie et al.<sup>20</sup> with a positive deviation of 22% at 268 K.

The kinetics of the  $\text{CH}_3\text{O}_2$  self-reaction has been studied coupling a FAGE instrument to HIRAC to carry out time-resolved measurements of the  $\text{CH}_3\text{O}_2$  concentrations during the reaction. Second-order decays of  $\text{CH}_3\text{O}_2$  were generated by turning the chamber lamps off. The observed rate coefficient at 295 K and 1000 mbar was  $k_{\text{obs}} = (2.7 \pm 0.9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Using  $k_{\text{obs}}(295 \text{ K}) = k_4(1 + r_{\text{CH}_3\text{O}})$  with  $r_{\text{CH}_3\text{O}}(\text{this work, 295 K}) = 0.34 \pm 0.05$  the second-order rate coefficient for the self-reaction at 295 K and 1000 mbar is  $k_4 = (2.0 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; employing the recommended value of 0.36 for  $r_{\text{CH}_3\text{O}}$  at 295 K by JPL<sup>6</sup> and IUPAC<sup>5</sup> does not change the result. The result at 295 K is  $\sim 40\%$  lower than the IUPAC and JPL recommendations:  $k_4 = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The temperature dependence of the overall rate coefficient can be parametrized as  $k_4 = (9.1 \pm 5.3) \times 10^{-14} \times \exp((252 \pm 174)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The present results have overlapping error limits at the  $2\sigma$  level with both JPL and IUPAC recommendations. However, on average the results of this work are  $\sim 40\%$  lower than the values calculated using the JPL<sup>6</sup> recommendation for the temperature dependence ( $k_4 = 9.5 \times 10^{-14} \times \exp(390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and the values obtained employing the temperature dependence recommended by IUPAC,<sup>5</sup>  $k_4 = 1.03 \times 10^{-13} \times \exp((365 \pm 200)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The previous kinetic studies utilized UV-absorption spectroscopy and may be impacted by secondary chemistry owing to the high radical concentrations generated in the reaction mixtures. Chemical modeling using the conditions of the previous studies and which included secondary chemistry of Cl species showed that the secondary chemistry increases the value of  $k_4$  obtained significantly. The FAGE method detects  $\text{CH}_3\text{O}_2$  sensitively, with a limit of detection of  $2.0 \times 10^9 \text{ molecules cm}^{-3}$  for a signal-to-noise ratio of 2, 1 s online averaging time, and 60 s offline averaging period. Therefore, the experiments reported here required a few orders of magnitude lower concentrations of  $\text{CH}_3\text{O}_2$  than  $[\text{CH}_3\text{O}_2]$  used in the UV-absorption studies and the impact of the secondary chemistry on the kinetic decays obtained by this work is negligible. In addition, the FAGE method probes  $\text{CH}_3\text{O}_2$  selectively, in the absence of any interference from other species.

Numerical models predict that  $\text{CH}_3\text{O}_2$  is the most abundant  $\text{RO}_2$  species in the atmosphere. Even though  $\text{CH}_3\text{O}_2$  has not been selectively measured in the atmosphere so far, its concentration at daytime has been estimated to peak in the range of daytime peak  $[\text{HO}_2]$ , i.e., at  $10^7$ – $10^8 \text{ molecules cm}^{-3}$ .<sup>43–45</sup> The atmospheric fate of  $\text{CH}_3\text{O}_2$  is typically dominated by the reaction with NO, with the  $\text{CH}_3\text{O}_2 + \text{HO}_2$  reaction becoming the main daytime loss of  $\text{CH}_3\text{O}_2$  under low  $\text{NO}_x$  levels. As  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  reach similar levels

at daytime and 298K,  $k_{\text{CH}_3\text{O}_2+\text{HO}_2}$  ( $5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is  $\sim 15$  times faster than the JPL and IUPAC recommendations for  $k_4$  ( $3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>5,6</sup> and  $\sim 25$  times higher than  $k_{4(\text{CH}_3\text{O}_2+\text{CH}_3\text{O}_2)}$  determined in this work ( $2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) the inclusion of the present  $k_{\text{obs}(\text{CH}_3\text{O}_2+\text{CH}_3\text{O}_2)}$  value in the atmospheric models might not impact significantly the daytime radical budget predicted by the models. However, at night-time it has been predicted that the self-reaction is the dominant removal of  $\text{CH}_3\text{O}_2$  due to a rapid loss of  $\text{HO}_2$  under dark conditions<sup>46</sup> and thus the atmospheric impacts of the present result need to be investigated.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c04968>.

Results of numerical simulations using a complex chemistry system and details of determination of the branching ratios in the  $\text{CH}_3\text{O}_2$  self-reaction as a function of temperature (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Dwayne E. Heard – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; [orcid.org/0000-0002-0357-6238](https://orcid.org/0000-0002-0357-6238); Phone: +44 113 343 6471; Email: [d.e.heard@leeds.ac.uk](mailto:d.e.heard@leeds.ac.uk)

### Authors

Lavinia Onel – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

Alexander Brennan – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

Freja F. Østerstrøm – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; Present Address: School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA and Department of Chemistry, University of Copenhagen, 2100 Copenhagen Ø, Denmark; [orcid.org/0000-0003-4125-3365](https://orcid.org/0000-0003-4125-3365)

Ellie Cooke – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

Lisa Whalley – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; National Centre for Atmospheric Science, University of Leeds, LS2 9JT, United Kingdom

Paul W. Seakins – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; [orcid.org/0000-0002-4335-8593](https://orcid.org/0000-0002-4335-8593)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jpca.2c04968>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors would like to thank the Natural Environment Research Council (NERC) for funding (grant reference NE/M011208/1) and the National Centre for Atmospheric Science. AB thanks to NERC for a studentship awarded in the framework of the SPHERES doctoral training programme (NE/L002574/1). F.F.Ø. thanks the Carlsberg Foundation for

support through the Carlsberg Foundation Internationalisation Fellowship, grant numbers CF16-0493 and CF17-0608.

## REFERENCES

- (1) Orlando, J. J.; Tyndall, G. S. Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance. *Chem. Soc. Rev.* **2012**, *41* (19), 6294–6317.
- (2) Kohse-Hoinghaus, K. Combustion in the future: The importance of chemistry. *Proc. Combust. Inst.* **2021**, *38* (1), 1–56.
- (3) Zador, J.; Taatjes, C. A.; Fernandes, R. X. Kinetics of elementary reactions in low-temperature autoignition chemistry. *Prog. Energy Combust.* **2011**, *37* (4), 371–421.
- (4) Tyndall, G. S.; Wallington, T. J.; Ball, J. C. FTIR product study of the reactions  $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{O}_2 + \text{O}_3$ . *J. Phys. Chem. A* **1998**, *102* (15), 2547–2554.
- (5) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species. *Atmos. Chem. Phys.* **2006**, *6*, 3625–4055.
- (6) Burkholder, J. B.; Sander, S. P.; Abbatt, J. P. D.; Barker, J. R.; Cappa, C.; Crounse, J. D.; Dibble, T. S.; Huie, R. E.; Kolb, C. E.; Kurylo, et al. Chemical kinetics and photochemical data for use in atmospheric studies - Evaluation number 19. available at <http://jpldataeval.jpl.nasa.gov/>, Access 10 May 2022.
- (7) Lightfoot, P. D.; Lesclaux, R.; Veyret, B. Flash photolysis study of the  $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$  reaction: Rate constants and branching ratios from 248 to 573 K. *J. Phys. Chem.* **1990**, *94* (2), 700–707.
- (8) Sander, S. P.; Watson, R. T. Kinetic studies of the reactions of  $\text{CH}_3\text{O}_2$  with  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{CH}_3\text{O}_2$  at 298 K. *J. Phys. Chem.* **1980**, *84* (13), 1664–1674.
- (9) McAdam, K.; Veyret, B.; Lesclaux, R. UV absorption spectra of  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  radicals and the kinetics of their mutual reactions at 298 K. *Chem. Phys. Lett.* **1987**, *133* (1), 39–44.
- (10) Kurylo, M. J.; Wallington, T. J. The temperature dependence of the rate constant for the gas phase disproportionation reaction of  $\text{CH}_3\text{O}_2$  radicals. *Chem. Phys. Lett.* **1987**, *138* (6), 543–547.
- (11) Sander, S. P.; Watson, R. T. Temperature dependence of the self-reaction of  $\text{CH}_3\text{O}_2$  radicals. *J. Phys. Chem.* **1981**, *85* (20), 2960–2964.
- (12) Cox, R. A.; Tyndall, G. S. Rate constants for the reactions of  $\text{CH}_3\text{O}_2$  with  $\text{HO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  using molecular modulation spectrometry. *J. Chem. Soc. Faraday Trans II* **1980**, *76*, 153–163.
- (13) Jenkin, M. E.; Cox, R. A.; Hayman, G. D.; Whyte, L. J. Kinetic study of the reactions  $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{O}_2 + \text{HO}_2$  using molecular modulation spectroscopy. *J. Chem. Soc. Faraday Trans. II* **1988**, *84*, 913–930.
- (14) Simon, F. G.; Schneider, W.; Moortgat, G. K. UV absorption spectrum of the methylperoxy radical and the kinetics of its disproportionation reaction at 300 K. *Int. J. Chem. Kinet.* **1990**, *22* (8), 791–812.
- (15) Tyndall, G. S.; Wallington, T. J.; Ball, J. C. FTIR product study of the reactions  $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{O}_2 + \text{O}_3$ . *J. Phys. Chem. A* **1998**, *102* (15), 2547–2554.
- (16) Weaver, J.; Meagher, J.; Shortridge, R.; Heicklen, J. Oxidation of acetyl radicals. *J. Photochem.* **1975**, *4* (5–6), 341–360.
- (17) Selby, K.; Waddington, D. J. Reactions of oxygenated radicals in the gas-phase 0.4. reactions of methylperoxyl and methoxyl radicals. *J. Chem. Soc.-Perkin Trans. 2* **1979**, *9*, 1259–1263.
- (18) Kan, C. S.; Calvert, J. G.; Shaw, J. H. Reactive channels of the  $\text{CH}_3\text{O}_2$ - $\text{CH}_3\text{O}_2$  reaction. *J. Phys. Chem.* **1980**, *84* (25), 3411–3417.
- (19) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. Fourier transform infrared studies of the self-reaction of  $\text{CH}_3\text{O}_2$  radicals. *J. Phys. Chem.* **1981**, *85* (7), 877–881.
- (20) Horie, O.; Crowley, J. N.; Moortgat, G. K. Methylperoxy self-reaction: Products and branching ratio between 223 and 333 K. *J. Phys. Chem.* **1990**, *94* (21), 8198–8203.
- (21) Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Pilling, M. J.; Ravishankara, A. R.; Wallington, T. J. Atmospheric chemistry of small organic peroxy radicals. *J. Geophys. Res.-Atmos.* **2001**, *106* (D11), 12157–12182.
- (22) Onel, L.; Brennan, A.; Seakins, P. W.; Whalley, L.; Heard, D. E. A new method for atmospheric detection of the  $\text{CH}_3\text{O}_2$  radical. *Atmos. Meas. Technol.* **2017**, *10* (10), 3985–4000.
- (23) Onel, L.; Brennan, A.; Gianella, M.; Hooper, J.; Ng, N.; Hancock, G.; Whalley, L.; Seakins, P. W.; Ritchie, G. A. D.; Heard, D. E. An intercomparison of  $\text{CH}_3\text{O}_2$  measurements by fluorescence assay by gas expansion and cavity ring-down spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry). *Atmos. Meas. Technol.* **2020**, *13* (5), 2441–2456.
- (24) Heard, D. E.; Pilling, M. J. Measurement of OH and  $\text{HO}_2$  in the troposphere. *Chem. Rev.* **2003**, *103* (12), 5163–5198.
- (25) Stone, D.; Whalley, L. K.; Heard, D. E. Tropospheric OH and  $\text{HO}_2$  radicals: field measurements and model comparisons. *Chem. Soc. Rev.* **2012**, *41* (19), 6348–6404.
- (26) Wang, G. Y.; Iradukunda, Y.; Shi, G. F.; Sanga, P.; Niu, X. L.; Wu, Z. J. Hydroxyl, hydroperoxyl free radicals determination methods in atmosphere and troposphere. *J. Environ. Sci.* **2021**, *99*, 324–335.
- (27) Glowacki, D. R.; Goddard, A.; Hemavibool, K.; Malkin, T. L.; Commane, R.; Anderson, F.; Bloss, W. J.; Heard, D. E.; Ingham, T.; Pilling, M. J.; et al. Design of and initial results from a Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC). *Atmospheric Chemistry and Physics* **2007**, *7* (20), 5371–5390.
- (28) Winiberg, F. A. F.; Smith, S. C.; Bejan, I.; Brumby, C. A.; Ingham, T.; Malkin, T. L.; Orr, S. C.; Heard, D. E.; Seakins, P. W. Pressure-dependent calibration of the OH and  $\text{HO}_2$  channels of a FAGE HOx instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC). *Atmos. Meas. Technol.* **2015**, *8* (2), 523–540.
- (29) Winiberg, F. A. F.; Dillon, T. J.; Orr, S. C.; Gross, C. B. M.; Bejan, I.; Brumby, C. A.; Evans, M. J.; Smith, S. C.; Heard, D. E.; Seakins, P. W. Direct measurements of OH and other product yields from the  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$  reaction. *Atmos. Chem. Phys.* **2016**, *16* (6), 4023–4042.
- (30) Onel, L.; Brennan, A.; Gianella, M.; Ronnie, G.; Aguila, A. L.; Hancock, G.; Whalley, L.; Seakins, P. W.; Ritchie, G. A. D.; Heard, D. E. An intercomparison of  $\text{HO}_2$  measurements by fluorescence assay by gas expansion and cavity ring-down spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry). *Atmos. Meas. Technol.* **2017**, *10* (12), 4877–4894.
- (31) Cantrell, C. A.; Zimmer, A.; Tyndall, G. S. Absorption cross sections for water vapor from 183 to 193 nm (vol 24, pg 2195, 1997). *Geophys. Res. Lett.* **1997**, *24* (21), 2687–2687.
- (32) Creasey, D. J.; Heard, D. E.; Lee, J. D. Absorption cross-section measurements of water vapour and oxygen at 185 nm. Implications for the calibration of field instruments to measure OH,  $\text{HO}_2$  and  $\text{RO}_2$  radicals. *Geophys. Res. Lett.* **2000**, *27* (11), 1651–1654.
- (33) Winiberg, F. A. F. Characterisation of FAGE apparatus for HOx detection and application in an environmental chamber, PhD. thesis. University of Leeds, Leeds, UK, 2014.
- (34) Maricq, M. M.; Szente, J. J.; Kaiser, E. W.; Shi, J. C. Reaction of chlorine atoms with methylperoxy and ethylperoxy radicals. *J. Phys. Chem.* **1994**, *98* (8), 2083–2089.
- (35) Jungkamp, T. P. W.; Kukui, A.; Schindler, R. N. Determination of rate constants and product branching ratios for the reactions of  $\text{CH}_3\text{O}_2$  and  $\text{CH}_3\text{O}$  with Cl atoms at room temperature. *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics* **1995**, *99* (8), 1057–1066.
- (36) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.; Wallington, T. J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV - gas phase reactions of organic halogen species. *Atmos. Chem. Phys.* **2008**, *8* (15), 4141–4496.
- (37) Hochanadel, C. J.; Ogren, P. J.; Ghormley, J. A. Absorption spectrum and reaction kinetics of  $\text{HO}_2$  radical in gas-phase. *J. Chem. Phys.* **1972**, *56* (9), 4426.

(38) Paukert, T. T.; Johnston, H. S. Spectra and kinetics of hydroperoxyl free radical in gas phase. *J. Chem. Phys.* **1972**, *56* (6), 2824–2838.

(39) Moortgat, G.; Veyret, B.; Lesclaux, R. Absorption spectrum and kinetics of reactions of the acetylperoxy radical. *J. Phys. Chem.* **1989**, *93* (6), 2362–2368.

(40) Dusanter, S.; Vimal, D.; Stevens, P. S. Technical note: Measuring tropospheric OH and HO<sub>2</sub> by laser-induced fluorescence at low pressure. A comparison of calibration techniques. *Atmos. Chem. Phys.* **2008**, *8* (2), 321–340.

(41) Schlosser, E.; Brauers, T.; Dorn, H. P.; Fuchs, H.; Haseler, R.; Hofzumahaus, A.; Holland, F.; Wahner, A.; Kanaya, Y.; Kajii, Y.; et al. Technical Note: Formal blind intercomparison of OH measurements: results from the international campaign HOxComp. *Atmospheric Chemistry and Physics* **2009**, *9* (20), 7923–7948.

(42) Fuchs, H.; Dorn, H. P.; Bachner, M.; Bohn, B.; Brauers, T.; Gomm, S.; Hofzumahaus, A.; Holland, F.; Nehr, S.; Rohrer, F.; T.; et al. Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration. *Atmos. Meas. Technol.* **2012**, *5* (7), 1611–1626.

(43) Whalley, L. K.; Edwards, P. M.; Furneaux, K. L.; Goddard, A.; Ingham, T.; Evans, M. J.; Stone, D.; Hopkins, J. R.; Jones, C. E.; Karunaharan, A.; et al. Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest. *Atmos. Chem. Phys.* **2011**, *11* (14), 7223–7233.

(44) Whalley, L. K.; Furneaux, K. L.; Goddard, A.; Lee, J. D.; Mahajan, A.; Oetjen, H.; Read, K. A.; Kaaden, N.; Carpenter, L. J.; Lewis, et al. The chemistry of OH and HO<sub>2</sub> radicals in the boundary layer over the tropical Atlantic Ocean. *Atmos. Chem. Phys.* **2010**, *10* (4), 1555–1576.

(45) Whalley, L. K.; Stone, D.; Dunmore, R.; Hamilton, J.; Hopkins, J. R.; Lee, J. D.; Lewis, A. C.; Williams, P.; Kleffmann, J.; Laufs, S.; et al. Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project (ClearfLo). *Atmos. Chem. Phys.* **2018**, *18* (4), 2547–2571.

(46) Monks, P. S.; Carpenter, L. J.; Penkett, S. A.; Ayers, G. P. Night-time peroxy radical chemistry in the remote marine boundary layer over the Southern ocean. *Geophys. Res. Lett.* **1996**, *23* (5), 535–538.