Acetonyl Peroxy and Hydro Peroxy Self- and Cross-Reactions: Kinetics, Mechanism, and Chaperone Enhancement from the Perspective of the Hydroxyl Radical Product

Zuraski, Kristen; Hui, Aileen O.; Grieman, Fred J.; Darby, Emily; Møller, Kristian H.; Winiberg, Frank A. F.; Percival, Carl J.; Smarte, Matthew D.; Okumura, Mitchio; Kjaergaard, Henrik G.; Sander, Stanley P.

Published in:

DOI:
10.1021/acs.jpca.0c06220

Publication date:
2020

Document version
Peer reviewed version

Document license:
CC BY

Citation for published version (APA):
Acetonyl Peroxy and Hydro Peroxy Self- and Cross-Reactions: Kinetics, Mechanism, and Chaperone Enhancement from the Perspective of the Hydroxyl Radical Product

Kristen Zuraski, Aileen O. Hui, Fred J. Grieman, Emily Darby, Kristian H. Møller, Frank A. F. Winiberg, Carl J. Percival, Matthew D. Smarte, Mitcho Okumura, Henrik Grum Kjaergaard, and Stanley P Sander

J. Phys. Chem. A, Just Accepted Manuscript • DOI: 10.1021/acs.jpca.0c06220 • Publication Date (Web): 27 Aug 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Acetonyl Peroxy and Hydro Peroxy Self- and Cross-Reactions: Kinetics, Mechanism, and Chaperone Enhancement from the Perspective of the Hydroxyl Radical Product

Kristen Zuraski, Aileen O. Hui, Fred J. Grieman, Emily Darby, Kristian H. Møller, Frank A. F. Winiberg, Carl J. Percival, Matthew D. Smarte, Mitchio Okumura, Henrik G. Kjaergaard, and Stanley P. Sander

aNASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, United States
bArthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States
cnow at: The Aerospace Corporation, El Segundo, California 90245, United States
dSeaver Chemistry Laboratory, Pomona College, Claremont, California 91711, United States
enow at: Trussell Technologies, Oakland, California 94612, United States
fDepartment of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

Corresponding Authors
*fjg04747@pomona.edu (F.J.G); hgk@chem.ku.dk (H.G.K); stanley.p.sander@jpl.nasa.gov (S.P.S.).
ABSTRACT

Pulsed laser photolysis coupled with infrared (IR) wavelength modulation spectroscopy and ultraviolet (UV) absorption spectroscopy was used to study the kinetics and branching fractions for the acetonyl peroxy (CH₃C(O)CH₂O₂) self-reaction and its reaction with hydro peroxy (HO₂) at a temperature of 298 K and pressure of 100 Torr. Near-IR and mid-IR lasers simultaneously monitored HO₂ and hydroxyl, OH, respectively, while UV absorption measurements monitored the CH₃C(O)CH₂O₂ concentrations. The overall rate constant for the reaction between CH₃C(O)CH₂O₂ and HO₂ was found to be $$(5.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$ and the branching fraction for OH yield from this reaction was directly measured as 0.30 ± 0.04. The CH₃C(O)CH₂O₂ self-reaction rate constant was measured to be $$(4.8 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$ and the branching fraction for alkoxy formation was inferred from secondary chemistry as 0.33 ± 0.13. An increase in the rate of the HO₂ self-reaction was also observed as a function of acetone (CH₃C(O)CH₃) concentration which is interpreted as a chaperone effect resulting from hydrogen-bond complexation between HO₂ and CH₃C(O)CH₃. The chaperone enhancement coefficient for CH₃C(O)CH₃ was determined to be $k''_A = (4.0 \pm 0.2) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and the equilibrium constant for HO₂•CH₃C(O)CH₃ complex formation was found to be $K_c(R15) = (2.0 \pm 0.89) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$; from these values the rate constant for the HO₂ + HO₂•CH₃C(O)CH₃ reaction was estimated to be $$(2 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$. Results from UV absorption cross-section measurements of CH₃C(O)CH₂O₂ and prompt OH radical yields arising from possible oxidation of the CH₃C(O)CH₃-derived alkyl radical are also discussed. Using theoretical methods, no likely pathways for the observed prompt OH radical formation have been found and thus remains unexplained.
I. INTRODUCTION

Atmospheric oxidation of volatile organic compounds (VOCs, RH) leads to the formation of organic peroxy radicals, RO₂. These species play a vital role in the budgets of O₃, NOₓ (NO + NO₂), NOᵧ (NOₓ + NO₂; NOₓ = HNO₃, HONO, PAN + other nitrogen oxides), and HOₓ (OH + HO₂) throughout the troposphere and, consequently, are important in determining atmospheric composition, the Earth’s radiative balance and future changes in climate. Once formed, RO₂ can react with NOₓ, HO₂ (R1), OH, other R’O₂ species/itself (R2), or undergo H-shift reactions to form autoxidation products (R3) as shown in Figure 1.1-10

Figure 1. General scheme for RO₂ chemistry in the atmosphere.¹, ² The right and left side represent low and high NOₓ environments, respectively. The bold arrow indicates unimolecular rearrangement by H-shift reactions.

In pristine environments, direct emissions from vegetation, oxidation of anthropogenic and biogenic hydrocarbons, oceans, and biomass burning make acetone, CH₃C(O)CH₃, one of the most abundant oxygenated VOCs in the atmosphere.¹¹-¹⁴ Following oxidation of CH₃C(O)CH₃ to form acetyl peroxy, CH₃C(O)CH₂O₂, reactions with hydro peroxy, HO₂, dominate in low NOₓ environments and impact the HOₓ balance by removing HO₂ and working as either a HOₓ radical sink through the formation of hydroperoxides (ROOH, R1a) or as radical
propagation by generating hydroxyl radicals (OH, R1b).\textsuperscript{15-21} The ozone generating pathway shown in Figure 1 is not available for CH$_3$C(O)CH$_2$O$_2$ due to the position of the carbonyl group.\textsuperscript{16}

\[
\begin{align*}
\text{HO}_2 + \text{CH}_3\text{C(O)CH}_2\text{O}_2 & \rightarrow \text{CH}_3\text{C(O)CH}_2\text{OOH} + \text{O}_2 \quad (R1a) \\
& \rightarrow \text{CH}_3\text{C(O)CH}_2\text{O} + \text{OH} + \text{O}_2 \quad (R1b)
\end{align*}
\]

The importance of accurately accounting for the OH production from peroxy radical reactions (R1b, in Fig. 1) is driven in part by OH field measurements in pristine environments which report elevated mixing ratios compared with atmospheric models.\textsuperscript{22-25} OH-recycling from peroxy radical reactions as well as autoxidation reactions may explain, in part, the discrepancy between measurements and models.

Additional fates of the CH$_3$C(O)CH$_2$O$_2$ radical in pristine environments include reactions with other peroxy radicals and with itself. These reactions are less dominating in the atmosphere compared to reactions with NO$_x$ and HO$_2$, but are important for laboratory studies. Similar to other peroxy radicals, there are two established self-reaction pathways for CH$_3$C(O)CH$_2$O$_2$: one which leads to hydroxyacetone (CH$_3$C(O)CH$_2$OH) and methylglyoxal (CH$_3$C(O)CHO) as stable products (R2a) and the other that generates acetonoxo radical (CH$_3$C(O)CH$_2$O, R2b).\textsuperscript{21, 26, 27} In addition, a third pathway, R2c, was recently proposed and observed by Berndt et al., which leads to higher functionalized accretion products, ROOR.\textsuperscript{28}

\[
\begin{align*}
2 \text{CH}_3\text{C(O)CH}_2\text{O}_2 & \rightarrow \text{CH}_3\text{C(O)CH}_2\text{OH} + \text{CH}_3\text{C(O)CHO} + \text{O}_2 \quad (R2a) \\
& \rightarrow 2 \text{CH}_3\text{C(O)CH}_2\text{O} + \text{O}_2 \quad (R2b) \\
& \rightarrow \text{C}_6\text{H}_{10}\text{O}_4 + \text{O}_2 \quad (\text{ROOR}) \quad (R2c)
\end{align*}
\]

Previously, the cross-reaction rate constant for CH$_3$C(O)CH$_2$O$_2$ + HO$_2$ ($k_1$) has only been measured once by Bridier et al.\textsuperscript{21} using flash photolysis and ultraviolet (UV) absorption of
CH$_3$C(O)CH$_2$O$_2$ and other radicals. As with all spectroscopic studies, the experimentally
determined rate constant is highly sensitive to the values of the UV absorption cross-sections
employed. However, the reported literature values of UV absorption cross-section for
CH$_3$C(O)CH$_2$O$_2$ radical, $\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$, are not in good agreement and vary by up to a factor of
2.5.\textsuperscript{21, 26, 29} The $k_1$ rate constant from the Bridier et al.\textsuperscript{21} study was determined using much larger
$\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$ values compared to other literature works. In subsequent studies, their value for $k_1$
was used to determine the branching fraction for OH formation,\textsuperscript{15, 18-20} which propagated any
error in their reported $k_1$ to the reported branching fraction values. The literature values for the
branching fraction of the OH generating channel, $k_{1b}/k_1$, are not in agreement, ranging from 0.15
– 0.67. A single theoretical study by Hasson et al.\textsuperscript{16} of the branching between R1a and R1b finds
that R1a is favored, but lowering the energy of the CH$_3$C(O)CH$_2$O$_2$$\cdot$HO$_2$ intermediate complex
by just 2 kcal mol$^{-1}$ inverts the branching to favor R1b demonstrating the sensitivity of the
branching fraction to the energies determined in the structure calculations. None of these
experimental or theoretical studies have considered H-shift isomerization reactions.

The rate constant for the CH$_3$C(O)CH$_2$O$_2$ self-reaction ($k_2$) has been measured by two
studies\textsuperscript{21, 26} that are in agreement but with one only reporting an upper limit\textsuperscript{26}. This agreement
may be fortuitous, however, because significantly different $\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$ were used between
these two studies. Subsequent indirect observation of the branching fraction of $k_{2b}/k_2$ by Emricha
and Warneck\textsuperscript{30} did not agree with the results by Bridier et al.\textsuperscript{21} showing a difference of 0.25. The
most recent results by Berndt et al.\textsuperscript{28} measured $k_{2c}$ only and based the branching fraction for this
channel on the results of the previous studies.

Our work is the first study to monitor simultaneously the time-dependent concentration
profiles for CH$_3$C(O)CH$_2$O$_2$, HO$_2$, and OH independently. The goal of this work is to reassess
and resolve the discrepancies in the overall kinetic rate constants, \( k_1 \) and \( k_2 \), and the associated branching fractions. We have re-measured \( \sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2} \) at selected wavelengths in the region between 290 – 320 nm and constrained the results of our kinetic model fits by coupling the kinetic data of \( \text{CH}_3\text{C(O)CH}_2\text{O}_2 \) with \( \text{HO}_2 \) and \( \text{OH} \), both obtained through infrared wavelength modulated spectroscopy (IR-WMS). In addition, a significant chaperone effect caused by \( \text{CH}_3\text{C(O)CH}_3 \) forming a hydrogen-bonded (H-bonded) complex with \( \text{HO}_2 \) that, in turn, increases the \( \text{HO}_2 \) self-reaction rate was also observed at room temperature and is reported here for the first time. This \( \text{HO}_2 \) self-reaction rate enhancement must be included in the analysis to obtain accurate kinetic parameters for the \( \text{CH}_3\text{C(O)CH}_2\text{O}_2 \) chemistry.

II. METHODS

IIa. Experimental

Infrared Kinetic Spectroscopy (IRKS)

Experiments conducted using the Infrared Kinetic Spectroscopy (IRKS) apparatus to study peroxy radical chemistry have been reported in earlier publications.\(^{31-33}\) Therefore, the method is discussed only briefly here with an emphasis on improvements in the detection capabilities and details specific to this work. The general schematic is shown in Figure 2.
Figure 2. Experimental schematic of the IRKS apparatus. M, D, H, and L are mirrors, dichroic filters, half-moon shaped Herriott mirrors, and lenses, respectively. The Herriott mirrors are housed inside nitrogen purged boxes attached to the jacketed cell. Solid Red lines represent the IR beam paths prior to entering the cell, the reflecting red lines in the cell represent thirty passes in a Herriott optic geometry, and the dashed red lines represent the IR beam paths after exiting the cell. The laser driven UV light source (LDLS) and 351 nm photolysis laser counter-propagated the cell entering/exiting the cell at a height offset but crossing the IR beam paths.

Pulsed laser photolysis (PLP) by a XeF excimer laser (Lambda Physik Compex 301, 351 nm, 110 mJ/pulse in constant energy mode, 0.2 Hz repetition rate) was used to initiate reactions in a continuous, temperature-controlled (T = 298 ± 1 K) flow cell (175 cm long, 5 cm diameter). The repetition rate of the photolysis laser was set to ensure products diffused out of the reaction volume between pulses and the flow cell pressure and temperature were held constant at 100 Torr and 298 K, respectively. Collimated broadband UV light generated by a laser driven light source (LDLS, Energetiq EQ-99XFC) counter propagated the excimer beam path through the cell and was separated from the excimer beam by a dichroic mirror and dispersed using a monochromator (Acton Research Corporation Spectra Pro-300i, slit width ~160 μm) coupled to a photomultiplier tube (EMI 9781A) for UV absorption measurements. The gas exit port positions (located in front of the Herriott mirrors, as shown in Figure 2) dictated the UV absorption...
pathlength, which was measured to be $148 \pm 10$ cm long by Cl$_2$ absorption at 320 nm ($\sigma_{\text{Cl}_2} = 2.37 \times 10^{-19}$ cm$^2$).$^{31}$

Two continuous-wave distributed feedback IR lasers (NASA JPL Microdevices Laboratory), were each wavelength modulated at 6.8 MHz, entered the cell through a hole in a custom coated mirror (Rocky Mountain Instrument Co.) aligned in a Herriott optical arrangement to achieve thirty passes through the cell, resulting in a total IR effective path length of approximately 27 m for each laser.$^{34}$ The Herriott mirrors were mounted inside nitrogen purged boxes attached to both ends of the cell as shown in Figure 2. After exiting the cell, the IR signals were detected independently using an indium gallium arsenide detector (InGaAs, New Focus 1811) and a liquid nitrogen-cooled indium antimonide detector (InSb, Infrared Associates IS-0.25) for the near- and mid-IR light, respectively. These signals were demodulated at 13.6 MHz and amplified by a factor of 200 for $2f$-heterodyne detection. Similar to previous works,$^{31-33}$ the concentrations derived from the $2f$ signals for both lasers detection axes were calibrated daily (See SI for details.).

In a typical experiment, the time-dependent UV absorption trace and the two IR kinetic traces were recorded simultaneously following the excimer photolysis pulse. Typical datasets comprised all three signals that were digitized and averaged for 800 excimer shots while simultaneously being recorded using NI LabVIEW software.

**Chemicals and Radical Generation**

Measured flows of nitrogen carrier gas (N$_2$, Airgas Corps., 99.997%) were bubbled through methanol (CH$_3$OH, Fisher Optima A454-1, $>99.9\%$) and acetone (CH$_3$C(O)CH$_3$, Fisher Optima A929-1, $>99.9\%$) to entrain these species in the gas phase. Changes in the bubbler flow rates were used to vary the concentrations of gaseous CH$_3$OH and CH$_3$C(O)CH$_3$. These
precursor gases were combined and premixed in a temperature-controlled glass manifold with 
chlorine (Cl₂, Air Products, 9.99% in He), oxygen (O₂, Airgas Corps., 99.996%), and N₂ (Airgas 
Corps., 99.997%) and then introduced through a central port of the flow cell (at the same 
temperature) depicted in Figure 2. Individual flow rates of the reaction precursors and the 
nitrogen bath gas were controlled using mass flow controllers (MKS Instruments). The total flow 
rate was 2160 sccm and the flow cell residence time was 9.7 s.

Photolysis of Cl₂ by pulsed 351 nm light generated atomic chlorine, Cl, to initiate 
reactions with CH₃C(O)CH₃ (R4) and CH₃OH (R6) to generate CH₃C(O)CH₂O₂ (R5) and HO₂ 
(R7), respectively, in the presence of O₂.

\[
\begin{align*}
\text{CH}_3\text{C(O)}\text{CH}_3 + \text{Cl} & \rightarrow \text{CH}_3\text{C(O)}\text{CH}_2 + \text{HCl} \\
\text{CH}_3\text{C(O)}\text{CH}_2 + \text{O}_2 (+\text{M}) & \rightarrow \text{CH}_3\text{C(O)}\text{CH}_2\text{O}_2 \\
\text{CH}_3\text{OH} + \text{Cl} & \rightarrow \text{CH}_2\text{OH} + \text{HCl} \\
\text{CH}_2\text{OH} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CH}_2\text{O}
\end{align*}
\]

Typical initial concentrations for investigating the cross-reaction, R1, averaged [Cl₂] = 9 – 10 × 
10^{15}, [Cl]₀ = 1 – 2 × 10^{14}, [CH₃OH] = 4 × 10^{15}, [CH₃C(O)CH₃] = 1.7 – 2.8 × 10^{16}, and [O₂] = 1.6 
× 10^{18} molecule cm⁻³ with N₂ added to achieve the total pressure. Concentrations of the 
precursors for observing R1 were set to have ratios of [HO₂]/[CH₃C(O)CH₂O₂] between 4 – 6 to 
keep HO₂ in excess of CH₃C(O)CH₂O₂ to reduce secondary chemistry from the CH₃C(O)CH₂O₂ 
self-reaction. Similar initial concentrations in the absence of CH₃OH were used for the UV 
cross-section measurements and for investigating R2.

Detection of Key Species

Combining the UV absorption and IR-WMS techniques makes this the first study to 
simultaneously monitor the time-dependent concentrations of CH₃C(O)CH₂O₂, HO₂, and OH
radicals. CH₃C(O)CH₂O₂ concentrations were detected by UV absorption spectroscopy using 312 nm light. At the same time, IR-WMS was used to monitor concentrations of HO₂ and the product OH at 6638.2 and 3407.6 cm⁻¹, respectively, via ro-vibrational lines. Under these experimental conditions, the normalized noise-equivalent sensitivity concentrations for the detection of HO₂ and OH radicals were on the order of 10⁸ molecule cm⁻³ Hz⁻¹/² (10⁹ molecule cm⁻³ for typical experiments).

IIb. Kinetic Modeling for Fitting Experimental Data

Because of the large number of reactions involved, numerical chemical simulations were necessary for extracting quantitative results for the rate constants and branching fractions of R1 and R2. A Python code adapted from an existing library³⁵ was used as a numerical integrator and fitting software encompassing the comprehensive mechanism shown in Table 1. The reaction list was constructed from a combination of the reactions listed in the JPL Data Evaluation 15-10 and relevant papers.¹⁸, ³³, ³⁶ CH₃C(O)CH₂O₂, HO₂, and OH kinetic data were fit simultaneously using a Levenberg-Marquardt algorithm³⁷, ³⁸ to optimize the kinetic rate constants and branching fractions against the datasets. Weights were applied to equalize the fitting across the different magnitudes of species concentrations. The fits were iterated 1000 times per experimental run following a Monte Carlo (MC) algorithm to randomly sample all parameters and systematic uncertainties (reaction rate constants and branching fractions, concentrations, calibration constants, the cell pathlength, Poisson counting in the data, and absorption cross sections) within each respective uncertainty. Initial guesses for the fitted parameters were sampled manually to ensure local minima were avoided. This procedure resulted in distributions of each fitted parameter from which its mean and uncertainty (reported as 1σ unless otherwise stated) could then be determined.
The self-reaction data (R2) was analyzed first. Here, OH and HO₂ kinetics are the result of secondary chemistry that is directly affected by the overall kinetic rate of R2 and the branching fraction R2b/R2 (discussed in section IIIb). The resulting fits determined the overall rate constant \( k_2 \) and the branching fraction, \( k_{2b}/k_2 \). In order to determine the rate constant and branching fraction for the cross-reaction, R1, the results of fitting R2 were incorporated into the model, and the experimental concentrations were set to minimize contributions from R2 by keeping HO₂ in excess of CH₃C(O)CH₂O₂ (\([\text{HO}_2]/[\text{CH}_3\text{C(O)CH}_2\text{O}_2] > 4\)). The sensitivity of the model for the cross-reaction to the rate of the self-reaction was tested and found to be negligible for the range \( k_2 = 3.5 - 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) under the conditions used in this work. The three [CH₃C(O)CH₂O₂], [HO₂] and [OH] time-dependent datasets were again fit simultaneously. For experimental runs of R1, the fitted parameters included \( k_{1a}, k_{1b} \), and the chaperone enhanced HO₂ self-reaction rate constant, \( k_{12,\text{obs}} \) (sections IIIb and IIIc). Following the determination of the fit parameters for the cross-reaction, these values were used to re-run the MC simulations for the self-reaction data to verify that the final values of \( k_2 \) and \( k_{2b}/k_2 \) were unaffected by the change in \( k_{1a}, k_{1b}, \) and \( k_{12,\text{obs}} \).

**Table 1.** Reaction scheme used in the determination of rates, branching fractions, and chaperone effects for the self- and cross-reactions of CH₃C(O)CH₂O₂ and HO₂. Rate constants are taken from the JPL Data Evaluation 15-10 recommended values[^36] and are all in cm³ molecule⁻¹ s⁻¹, unless indicated otherwise. Uncertainties in values are given in their respective references.

<table>
<thead>
<tr>
<th>( k )</th>
<th>Reaction</th>
<th>Branching Ratio</th>
<th>Rate Constant</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Radical Reactant Generation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_6 )</td>
<td>( \text{CH}_3\text{OH} + \text{Cl} \rightarrow \text{CH}_2\text{OH} + \text{HCl} )</td>
<td></td>
<td>( 5.5 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>( k_7 )</td>
<td>( \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{O} )</td>
<td></td>
<td>( 9.1 \times 10^{-12} )</td>
<td></td>
</tr>
<tr>
<td>( k_4 )</td>
<td>( \text{CH}_3\text{C(O)CH}_3 + \text{Cl} \rightarrow \text{CH}_3\text{C(O)CH}_2 + \text{HCl} )</td>
<td></td>
<td>( 1.63 \times 10^{-11} \text{ exp}(-610/\text{T}) )</td>
<td></td>
</tr>
<tr>
<td>( k_{5a} )</td>
<td>( \text{CH}_3\text{C(O)CH}_2 + \text{O}_2 (+\text{M}) \rightarrow \text{CH}_3\text{C(O)CH}_2\text{O}_2 )</td>
<td>( 0.98 )</td>
<td>( 2.75 \times 10^{-31}[\text{M}] )</td>
<td></td>
</tr>
<tr>
<td>( k_{5b} )</td>
<td>( \text{CH}_3\text{C(O)CH}_2 + \text{O}_2 (+\text{M}) \rightarrow \text{OH} + \text{products} )</td>
<td>( 0.01 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_{5c} )</td>
<td>( \text{CH}_3\text{C(O)CH}_2 + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 + \text{products} )</td>
<td>( 0.01 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Primary Chemistry

<table>
<thead>
<tr>
<th>$k_{12}$</th>
<th>$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$</th>
<th>$1.5 \times 10^{-12} + 4.0 \times 10^{-29} \times [CH_3C(O)CH_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{2a}$</td>
<td>$2CH_3C(0)CH_2O \rightarrow CH_3C(0)CHO + CH_3C(0)CH_2OH + O_2$</td>
<td>$4.8 \times 10^{-12}$</td>
</tr>
<tr>
<td>$k_{2b}$</td>
<td>$2CH_3C(0)CH_2O \rightarrow 2 CH_3C(0)CH_2O + O_2$</td>
<td>$0.68$</td>
</tr>
<tr>
<td>$k_{2c}$</td>
<td>$2CH_3C(0)CH_2O \rightarrow$ accretion products</td>
<td></td>
</tr>
<tr>
<td>$k_{1a}$</td>
<td>$HO_2 + CH_3C(O)CH_2O \rightarrow CH_3C(O)CH_2OOH + O_2$</td>
<td>$0.70 \times 5.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>$k_{1b}$</td>
<td>$HO_2 + CH_3C(O)CH_2O \rightarrow CH_3C(O)CH_3O + OH + O_2$</td>
<td>$0.30$</td>
</tr>
</tbody>
</table>

### Secondary Chemistry

<table>
<thead>
<tr>
<th>$k_{11}$</th>
<th>$Cl + HO_2 \rightarrow OH + ClO$</th>
<th>$3.6 \times 10^{-11} \exp(-375/T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cl + HO_2 \rightarrow O_2 + HCl$</td>
<td>$1.4 \times 10^{-11} \exp(270/T)$</td>
<td></td>
</tr>
<tr>
<td>$2 CH_3O_2 \rightarrow 2 CH_3O + O_2$</td>
<td>$0.59 \times 3.5 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>$2 CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$</td>
<td>$0.41$</td>
<td></td>
</tr>
<tr>
<td>$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$</td>
<td>$0.9 \times 5.2 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>$HO_2 + CH_3O_2 \rightarrow CH_2O + H_2O + O_2$</td>
<td>$0.1$</td>
<td></td>
</tr>
<tr>
<td>$OH + CH_3OOH \rightarrow$ products</td>
<td>$3.8 \times 10^{-12} \exp(200/T)$</td>
<td></td>
</tr>
<tr>
<td>$CH_3O + O_2 \rightarrow CH_2O + HO_2$</td>
<td>$3.9 \times 10^{-14} \exp(-900/T)$</td>
<td></td>
</tr>
<tr>
<td>$O + CH_3O \rightarrow$ products</td>
<td>$3.4 \times 10^{-11} \exp(-1600/T)$</td>
<td></td>
</tr>
<tr>
<td>$OH + CH_3O \rightarrow H_2O + HCO$</td>
<td>$5.5 \times 10^{-12} \exp(125/T)$</td>
<td></td>
</tr>
<tr>
<td>$HO_2 + CH_3O \rightarrow HOCH_2O_2$</td>
<td>$6.7 \times 10^{-15} \exp(600/T)$</td>
<td></td>
</tr>
<tr>
<td>$CH_3 + O_2 (+M) \rightarrow CH_3O_2$</td>
<td>$1.16 \times 10^{-31} \text{[M]}$</td>
<td></td>
</tr>
<tr>
<td>$CH_3O_2 + CH_3C(O)CH_2O \rightarrow CH_3C(O)CH_2O + CH_3O + O_2$</td>
<td>$0.3 \times 7.5 \times 10^{-13} \exp(500/T)$</td>
<td></td>
</tr>
<tr>
<td>$CH_3O_2 + CH_3C(O)CH_2O \rightarrow CH_3C(O)CH_2O + CH_3OH + CH_2O + O_2$</td>
<td>$0.2$</td>
<td></td>
</tr>
<tr>
<td>$CH_3O_2 + CH_3C(O)CH_2O \rightarrow CH_3C(O)CHO + CH_3OH + O_2$</td>
<td>$0.5$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$k_{10}$</th>
<th>$CH_3C(O)CH_2O + O_2 \rightarrow CH_3C(O)CHO + HO_2$</th>
<th>$9.7 \times 10^{-15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_8$</td>
<td>$CH_3C(O)CH_2O \rightarrow CH_3CO + CH_2O$</td>
<td>rapid</td>
</tr>
<tr>
<td>$OH + HO_2 \rightarrow H_2O + O_2$</td>
<td>$4.8 \times 10^{-11} \exp(250/T)$</td>
<td></td>
</tr>
<tr>
<td>$O + O_2 (+M) \rightarrow O_3$</td>
<td>$6.10 \times 10^{-24} \text{[M]}$</td>
<td></td>
</tr>
<tr>
<td>$OH + HCl \rightarrow H_2O + Cl$</td>
<td>$1.8 \times 10^{-12} \exp(-250/T)$</td>
<td></td>
</tr>
<tr>
<td>$k_{9a}$</td>
<td>$CH_3CO + O_2 (+M) \rightarrow CH_3C(O)O_2$</td>
<td>$0.97 \times 3.99 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
IIc. THEORETICAL METHODS AND ENERGETICS

The potential for OH recycling via unimolecular reactions following O$_2$-addition to the acetonyl radical was modelled using a Rice-Ramsperger-Kassel-Marcus (RRKM) master equation (ME) approach reflecting the experimental conditions. The energetics are calculated as described in the approach by Møller et al.$^{44}$ and briefly outlined here. Conformers of reactants, transition states (TSs) and products are sampled using MMFF in Spartan '18 based on optimized structures at the B3LYP/6-31+G(d) level from Gaussian 16, rev. C.01.$^{45-52}$ For the transition states, suitable bond lengths are constrained in the conformer sampling. The resulting conformers are optimized at the B3LYP/6-31+G(d) level in Gaussian 16.$^{50}$ Unique conformers$^{44,53}$ within 2 kcal mol$^{-1}$ in electronic energy of the lowest energy conformer are further optimized at the ωB97X-D/aug-cc-pVTZ level$^{54-57}$ in Gaussian 16. For the conformer lowest in zero-point corrected electronic energy at this level, an RO-CCSD(T)-F12a/VDZ-F12 single-point calculation is done in Molpro2012.$^{58-63}$ The reactions are modelled using the Master Equation Solver for Multi Energy-well Reactions (MESMER)$^{63}$ based on the ωB97X-D/aug-cc-pVTZ thermodynamic properties of the lowest-energy conformers and improved using the RO-

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>$k_{\text{b}}$</th>
<th>$k_{\text{c}}$</th>
<th>$k_{\text{ac}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{OH} + \text{products}$</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{products}$</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{C(O)}\text{OOH} + \text{O}_2$</td>
<td>0.29</td>
<td>$1.72 \times 10^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HO}_2^* + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{C(O)}\text{OH} + \text{O}_3$</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HO}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{OH} + \text{CH}_3\text{CO}_2 + \text{O}_2$</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{CO}_2 + \text{CH}_3\text{O} + \text{O}_2$</td>
<td>0.9</td>
<td>$2.0 \times 10^{-12}$ exp(500/T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{C(O)}\text{OH} + \text{CH}_3\text{O} + \text{O}_2$</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}_2 \rightarrow \text{CH}_3 + \text{CO}_2$</td>
<td>rapid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(O)CH}_2\text{O}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{C(O)CH}_2\text{O} + \text{CH}_3\text{CO}_2 + \text{O}_2$</td>
<td>0.5</td>
<td>$5.0 \times 10^{-12}$</td>
<td>21,41</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(O)CH}_2\text{O}_2 + \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{C(O)CHO} + \text{CH}_3\text{C(O)}\text{OH} + \text{O}_2$</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2 \text{CH}_3\text{C(O)}\text{O}_2 \rightarrow \text{CH}_3\text{CO}_2 + \text{O}_2 + \text{CH}_3\text{CO}_2$</td>
<td>$2.9 \times 10^{-12}$ exp(500/T)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HOCH}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 + \text{HOCH}_2\text{O}$</td>
<td>$5.6 \times 10^{-15}$ exp(2300/T)</td>
<td></td>
<td>42,43</td>
<td></td>
</tr>
</tbody>
</table>
CCSD(T)-F12a/VDZ-F12//ωB97X-D/aug-cc-pVTZ electronic energies. Further details of the MESMER modelling are given in the Supplemental Information (SI) Section SII. The rate coefficients for the unimolecular reactions of the thermalized species modelled are further calculated using the multi-conformer transition state theory (MC-TST) approach by Møller et al.\textsuperscript{44} including the Eckart tunneling correction.\textsuperscript{64} Rate coefficients of additional possible unimolecular reactions from subsequent intermediates were calculated at the same level of theory to aid the analysis of the experimental results (Section SIII in SI). All calculations are done at 298.15K.

III. RESULTS

IIIa. CH$_3$C(O)CH$_2$O$_2$ UV Absorption Cross-Section

The inset in Figure 3 displays a typical set of UV absorption data used to assess $\sigma_{\text{CH$_3$C(O)CH$_2$O$_2$}}$ in the spectral region $\lambda = 290 – 320$ nm for select wavelengths (see SV in SI for complete data set). Experimental parameters were held constant as the monochromator grating position scanned across the spectral window in 5 nm steps. CH$_3$C(O)CH$_2$O$_2$ is a transient species, therefore, the reaction kinetics are coupled to quantifying $\sigma_{\text{CH$_3$C(O)CH$_2$O$_2$}}$. Kinetic modeling was used to determine the time window for applying the fit at early times (0 – 2 ms) representative of second-order kinetics. The time window for the fit was optimized to exclude (1) scattered light and fluorescence from the excimer pulse which saturates the probe beam detector at early times ($t < 0.2$ ms), and (2) the influence of absorption from secondary species that absorb in this spectral region at later times (see SIV in SI for details). The inverse absorbance, 1/Abs, vs. time was used under the assumption of second-order analysis in this time range. The integrated rate law for second-order kinetics dictates that a linear fit corresponds to Equation 1

\[
\frac{1}{\text{Abs}} = \frac{2k_2l}{\sigma_{\text{CH$_3$C(O)CH$_2$O$_2$}}} + \frac{1}{[\text{CH$_3$C(O)CH$_2$O$_2$}]_0\sigma_{\text{CH$_3$C(O)CH$_2$O$_2$}}} \tag{E1}
\]
where \( l \) is the pathlength of the absorption measurement, \( k_2 \) is the bimolecular rate constant for R2, and \([\text{CH}_3\text{C(O)CH}_2\text{O}_2]_0\) is the initial concentration of \( \text{CH}_3\text{C(O)CH}_2\text{O}_2 \) formed at \( t = 0 \) s following reaction of the radical precursors. \([\text{CH}_3\text{C(O)CH}_2\text{O}_2]_0\) was equated with \([\text{Cl}]_0\) determined during the calibration experiments (see SI for details). In the absence of \( \text{CH}_3\text{OH} \) to form \( \text{HO}_2 \), the same initial concentration of \( \text{CH}_3\text{C(O)CH}_2\text{O}_2 \) forms under the condition of constant excimer power and \([\text{Cl}]_0\). The y-intercept from the linear fit was used to calculate the value of \( \sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2} \) using E1. Our results are shown in Table 2 and Figure 4 with comparison to prior studies.\(^{21, 26, 29, 36}\) The reported uncertainties were calculated through propagation of error and include the uncertainty in the linear fit, the pathlength, and the determined initial concentrations.

**Figure 3.** UV 1/Abs vs. time measurements obtained for \( \text{CH}_3\text{C(O)CH}_3/\text{Cl}_2/\text{O}_2/\text{N}_2 \) mixtures under conditions of constant laser power and \([\text{Cl}_2]\) to observe the \( \text{CH}_3\text{C(O)CH}_2\text{O}_2 \) self-reaction. Each UV time trace shown in the inset for selected wavelengths in the range \( \lambda = 290 – 320 \text{ nm} \) was converted to 1/Abs and fit with a linear regression following second order kinetics in the 0.6 – 2 ms range. Additional datasets are shown in Figure S8 in the SI.
Table 2: Absorption cross-sections of CH$_3$C(O)CH$_2$O$_2$, $\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$, measured at $T = 298 (\pm 1)$ K and $P = 100 (\pm 1)$ Torr. Propagation of error for the reported uncertainties accounts for the uncertainties in the fits, pathlength, and initial radical concentrations.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$10^{20} \sigma$ (cm$^2$ molecule$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>212 ($\pm$38)</td>
</tr>
<tr>
<td>295</td>
<td>196 ($\pm$32)</td>
</tr>
<tr>
<td>300</td>
<td>192 ($\pm$31)</td>
</tr>
<tr>
<td>305</td>
<td>166 ($\pm$23)</td>
</tr>
<tr>
<td>310</td>
<td>164 ($\pm$22)</td>
</tr>
<tr>
<td>315</td>
<td>163 ($\pm$22)</td>
</tr>
<tr>
<td>320</td>
<td>141 ($\pm$17)</td>
</tr>
</tbody>
</table>

Figure 4. Comparison of the CH$_3$C(O)CH$_2$O$_2$ cross-section, $\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$, measured from this work (red squares), Bridier et al. (circles),$^{21}$ Cox et al. (squares),$^{26}$ Nielsen et al. ($\times$),$^{29}$ and the recommended values by JPL Evaluation 15-10 (diamonds)$^{35}$ which reports the cross-section values from Cox et al. re-normalized to the absolute value at 240 nm measured by Nielsen et al. Errors in literature cross-section values were not available for all of the previous works as shown.

IIIb. CH$_3$C(O)CH$_2$O$_2$ self-reaction kinetics
Figure 5 shows comparisons between experimental data and the kinetic model using the IUPAC$^{66}$ recommended value of $k_2$, $8.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, vs. the value for $k_2$ determined from our MC simulations, $4.8 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. As is clearly seen, the recommended value for $k_2$ does not capture the CH$_3$C(O)CH$_2$O$_2$ kinetics observed in our experiments. Although Equation 1 could be used to determine the effective rate constant for R2 using the slope of the linear fit, it would result in large experimental uncertainty as a result of fitting only over a narrow temporal window. Fitting only CH$_3$C(O)CH$_2$O$_2$ would also leave determination of $k_2$ less constrained. To overcome these deficiencies, the concentration time profiles of HO$_2$ and OH were fit simultaneously with the CH$_3$C(O)CH$_2$O$_2$ radical kinetics using the MC simulation fitting method and model mechanism described in Section IIb and the absorption cross-sections given in Table 2. The time windows for the fits were 0.6 – 4, 0 – 20, and 0 – 2 ms for the CH$_3$C(O)CH$_2$O$_2$, HO$_2$, and OH kinetic traces, respectively, in order to disregard the early times for the UV data (<0.2 ms) that are affected by the excimer laser and data from later times to minimize higher contributions from secondary chemistry for each species.
Figure 5. Experimental data (red) for [CH₃C(O)CH₂O₂] vs. time obtained by UV absorption measurements at 312 nm using linear interpolation of the 310 and 315 nm UV cross-sections determined in this work (Table 2). The kinetic simulation generated with recommended rate parameters for \(k_2\) and \(k_{2b} / k_2\) by IUPAC is shown in turquoise and the fit from the MC simulations is shown in black.

Figure 6a and 6b show the experimental vs. simulated time-dependent HO₂ and OH concentrations, respectively, where the simulated kinetic profiles for each species using the IUPAC recommended values are shown in turquoise. Results of this work, where \(k_2\) and \(k_{2b} / k_2\) were fit to the experimental data, are shown in black in Figure 6 and histograms representing the occurrences for the \(k_2\) and \(k_{2b} / k_2\) parameters from the MC simulations are shown in Figure 7. The magnitudes of both the OH and HO₂ simulated kinetic concentrations, shown in Figure 6, were extremely sensitive to the branching fraction for CH₃C(O)CH₂O formation, \(R_{2b}\) in the mechanism. The use of the IUPAC recommended value for the branching fraction, \(k_{2b} / k_2 = 0.63 (± 0.20)\), overpredicted our experimental observations for the HO₂ and OH concentrations by a factor of ~2. Fitting the experimental data yielded a branching fraction of \(k_{2b} / k_2 = 0.33 (± 0.13)\) and dramatically reduced the discrepancies between the kinetic model and our data.

Figure 6. Experimental (red) and calculated kinetic profiles for (a) HO₂ and (b) OH for the CH₃C(O)CH₂O₂ self-reaction. The kinetic model (turquoise) shows the simulated concentrations using the IUPAC recommended rate parameters and the results of the fit (black) shows the simulated concentrations with the parameters from this work. The dashed blue lines show (a) the fit without \(k_9\) adjustment (see text) and (b) the model simulated with prompt OH arising from the acetonyl + O₂ reaction (see text) for comparison. The uncertainties in the experimentally
measured HO₂ and OH concentrations were ± 3.2 × 10^{10} and ± 1.4 × 10^9 molecules cm^{-3}, respectively.

![Histogram output from the MC simulations (4000 iterations)](image)

**Figure 7.** Histogram output from the MC simulations (4000 iterations) for (a) $k_2 = (4.8 \pm 0.8) \times 10^{-12}$ cm³ molecule^{-1} s^{-1} and (b) $k_{2b} / k_2 = 0.33 \pm 0.13$.

The fit in Figure 5 was primarily dependent on the absolute concentration of the CH₃C(O)CH₂O product formation through the R2b channel as opposed to the relative product formation between R2b and the other reaction pathways as discussed in Section IIIa. Equivalent fits to that shown in Figure 6 were achieved when maintaining a branching fraction for R2b pathway of 0.33 (± 0.13) with any combined remaining branching fraction of the R2a + R2c. Therefore, our experiments cannot distinguish between the other two channels, R2a and R2c. However, the recent mass-spectrometry study by Berndt et al.²⁸ observed and proposed a mechanism for a third channel, R2c, for the CH₃C(O)CH₂O self-reaction which leads to accretion product formation (ROOR) with a rate constant of $1.3 \times 10^{-12}$ cm³ molecule^{-1} s^{-1}. Their results inferred a product branching fraction at 295 K for R2c of 0.16 based on the recommended overall $k_2$. Based on their rate constant for R2c and $k_2$ determined in this work, a larger branching fraction for the R2c accretion product channel of 0.30 was calculated.

Monitoring the HO₂ and OH concentrations constrained the fit for the rate constant and branching fractions while also providing insight to the secondary chemistry arising from R2. The secondary chemistry is complex; however, the difference in the chemical timescales for the
modeled reaction mechanism in comparison to the experimental data enabled the
characterization of the experimentally observed HO2 and OH concentrations. A possible
explanation for the relationship between the time-dependent HO2 and OH concentrations and the
magnitude of the branching fraction involve the subsequent alkoxy product chemistry. Here, the
CH3C(O)CH2O product formation rapidly decomposes to the acetyl, CH3CO, product (R8)
which is oxidized to form acetyl peroxy, CH3C(O)O2 (R9a), OH (R9b) and HO2 (R9c).39

\[
\begin{align*}
\text{CH}_3\text{C(O)CH}_2\text{O} & \rightarrow \text{CH}_3\text{CO} + \text{CH}_2\text{O} & \text{(R8)} \\
\text{CH}_3\text{CO} + \text{O}_2 & \rightarrow \text{CH}_3\text{C(O)O}_2 & \text{(R9a)} \\
& \rightarrow \text{OH} + \text{products} & \text{(R9b)} \\
& \rightarrow \text{HO}_2 + \text{products} & \text{(R9c)}
\end{align*}
\]

To achieve the calculated kinetic profiles for the fits shown in Figure 6, two rate
parameters had to be adjusted relative to the recommended values shown in Table 1 in addition
to fitting the overall CH3C(O)CH2O2 self-reaction kinetic parameters. First, there was a
significant absence of prompt OH being formed in the calculated model at early times (<0.2 ms).
Augmenting the oxygenation reaction of the alkyl group (acetonyl, CH3C(O)CH2) in the initial
formation of CH3C(O)CH2O2 to include 0.02 ± 0.01 product OH formation (R5b) affected the
calculated model as shown by the dashed blue line in Figure 6b.

\[
\begin{align*}
\text{CH}_3\text{C(O)CH}_2 + \text{O}_2 (+\text{M}) & \rightarrow \text{CH}_3\text{C(O)CH}_2\text{O}_2 (+\text{M}) & \text{(R5a)} \\
\text{CH}_3\text{C(O)CH}_2 + \text{O}_2 (+\text{M}) & \rightarrow \text{OH} + \text{products} (+\text{M}) & \text{(R5b)}
\end{align*}
\]

The mechanism for the proposed OH formation is not resolved and further discussion of the
validity of this alkyl chemistry is discussed in section IV. Due to the timescale of the prompt
OH, the inclusion of prompt OH formation mechanism did not affect the fit for the branching
fraction, \( k_{2b} / k_2 \). The second parameter that was adjusted was the rate constant \( k_9 \) corresponding to reaction between CH\(_3\)C(O)CH\(_2\)O and O\(_2\) (R10).

\[
\text{CH}_3\text{C(O)CH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)CHO} + \text{HO}_2 \quad (\text{R10})
\]

This reaction was shown to affect the calculated HO\(_2\) concentrations on the time scales between 0 – 5 ms, as shown in Figure 6a (dashed blue). Increasing the rate constant by a factor of two greatly improved the fit to the experimental data. As this rate constant is relatively small compared to the decomposition pathway (R8), this adjustment did not have a significant effect on the other observed species concentration time profiles.

### IIIc. CH\(_3\)C(O)CH\(_2\)O\(_2\) + HO\(_2\): Rate Constant and Branching Fraction

Figure 8 shows a representative dataset for concentration profiles of HO\(_2\), CH\(_3\)C(O)CH\(_2\)O\(_2\), and OH arising from the cross-reaction between CH\(_3\)C(O)CH\(_2\)O\(_2\) and HO\(_2\) (R1). The simulated kinetics using the IUPAC recommended values\(^{66}\) is also shown in comparison to the results of the MC simulation fits obtained in this work. Unlike the CH\(_3\)C(O)CH\(_2\)O\(_2\) self-reaction study, HO\(_2\) and OH are a primary reactant and product, respectively, and determining the branching fraction for the OH channel, R1b, is more straightforward. Figure 8a shows the HO\(_2\) concentration time dependence, which is in excess over CH\(_3\)C(O)CH\(_2\)O\(_2\) concentrations by a factor of 4 – 6. It is the least sensitive of the three species to changes in \( k_1 \) because the difference between the kinetic model with the IUPAC\(^{66}\) recommended values and the fit values for the HO\(_2\) kinetic profile arises primarily from the CH\(_3\)C(O)CH\(_3\) rate enhancement coefficient for the HO\(_2\) self-reaction (discussed in detail in Section IIIId).

Figure 8b shows the CH\(_3\)C(O)CH\(_2\)O\(_2\) concentration time dependence, which was monitored using UV absorption at 312 nm, and Figure 8c shows the OH concentration kinetics,
which was monitored using IR-WMS; both are compared to the IUPAC modeled and out fitted kinetics. In the cross-reaction, as in the experimental results for the CH$_3$C(O)CH$_2$O$_2$ self-reaction, the prompt OH signal at early times is observable and in our fitted kinetics is simulated as arising from R5b in the mechanism. In the presence of HO$_2$, there is an additional prompt OH concentration source present for the cross-reaction arising at early times from the reaction between HO$_2$ and Cl (R11).

\[ \text{HO}_2 + \text{Cl} \rightarrow \text{OH} + \text{ClO} \]  
(R11)

However, the additional OH at early times from R11 does not generate enough prompt OH to fit the data. A branching fraction of 0.02 ± 0.01 for R5b again fits the prompt OH kinetics as shown in Figure 8c. The fit for the branching fraction was observable in the OH kinetics as a scaling of the OH concentrations on the timescale immediately following the prompt OH formation and was, therefore, not influenced by the inclusion of the prompt OH formation mechanism. The rate constant, $k_1$, and branching fraction for the OH channel, $k_{1b}/k_1$, were determined from the MC fitting to be $(5.5 \pm 0.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $0.30 \pm 0.04$, respectively. The uncertainties in our reported values were determined from a series of MC simulations as described in section IIB; a representative set of histograms for the $k_1$ and $k_{1b}/k_1$ are shown in Figure 9a and 9b, respectively. The resulting fits using these parameters are compared in Figure 8 to the model results using the currently recommended values$^{36,66}$: $k_1 = 9.0 \ (\pm 1.0) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{1b}/k_1 = 0.15 \pm 0.10$. The improved agreement is clearly observable.
Figure 8. Experimental (a) HO$_2$, (b) CH$_3$C(O)CH$_2$O$_2$, and (c) OH time-dependent concentrations (red) for the HO$_2$ + CH$_3$C(O)CH$_2$O$_2$ reaction. Uncertainties in the measured HO$_2$ and OH concentrations were $\pm 1.6 \times 10^{10}$ and $3.5 \times 10^8$ molecules cm$^{-3}$, respectively. The simulated concentrations using recommended rate parameters by IUPAC$^{66}$ (turquoise) are shown in all three panels. In panel (c) inclusion of the prompt OH (see text) is displayed (blue dashed) for comparison. The results of the fits of the temporal concentrations with the parameters from this work (black) are shown in all three panels.

Figure 9. Histogram output from the MC simulations (4000 iterations) for (a) $k_1 = (5.5 \pm 0.5) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and (b) $k_{1b} / k_1 = 0.30 \pm 0.04$.

IIIid. HO$_2$ + HO$_2$: Chaperone Effects by CH$_3$OH and CH$_3$C(O)CH$_3$

A chaperone effect, increasing the rate of the self-reaction for HO$_2$ (R12) via H-bonded complex formation, was observed in this work.

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]  

(R12)

Because a change in the effective rate constant for the HO$_2$ self-reaction, $k_{12,\text{obs}}$, impacts the retrieved rate constants for R1 and R2,\textsuperscript{31,67,68} it was necessary to assess its impact quantitatively in this study.
The chaperone rate enhancing effect by CH₃OH on R₁₂, resulting from forming HO₂•CH₃OH has been studied previously⁶⁷-⁶⁹ and is due to the increased reaction rate of R₁₃ compared to R₁₂.

\[
\text{HO}_2 + \text{HO}_2\cdot\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{CH}_3\text{OH} \quad (\text{R}13)
\]

It was shown to be negligible at room temperature and under the concentration conditions used in this work because, in part, the equilibrium constant for complexation, \(K_c(R14)\) is small (\(1.0 \times 10^{-18}\) cm³ molecule⁻¹) at room temperature.³⁶

\[
\text{HO}_2 + \text{CH}_3\text{OH} \rightleftharpoons \text{HO}_2\cdot\text{CH}_3\text{OH} \quad (\text{R}14)
\]

To test for the effect of CH₃OH chaperone, we conducted experiments in the absence of CH₃C(O)CH₃ while varying the CH₃OH concentration (see SI for details). We verify that the chaperone effect from HO₂•CH₃OH was negligible. For the purpose of this work, the JPL recommended value³⁶ for \(k_{12}\) (\(1.55 \times 10^{-12}\) cm³ molecule⁻¹ s⁻¹) was used.

CH₃C(O)CH₃ forms a strong bond with HO₂ and its chaperone effect could be significant at room temperature. Determining the effect of HO₂•CH₃C(O)CH₃ complexation on \(k_{12}\) is complicated by the secondary CH₃C(O)CH₂O₂ peroxy radical chemistry. The fraction of HO₂ complexed as HO₂•CH₃C(O)CH₃ was included in the kinetic mechanism. The observed rate of \(R₁₂, k_{12,\text{obs}}\), in the presence of CH₃C(O)CH₃ was also allowed to vary during the MC simulations for determining the cross-reaction rate \(k_1\) and branching fraction \(k_{1b}/k_1\) for R₁. We found \(k_{12,\text{obs}}\) to be statistically greater than the recommended value for \(k_{12}\).

To test the possible chaperone enhancement by CH₃C(O)CH₃ at room temperature, a series of experiments were conducted as a function of CH₃C(O)CH₃ concentration with all other experimental parameters held constant. The results, shown in Figure 10, are reported as the first observation of the chaperone effect rate enhancement on \(k_{12}\) at room temperature resulting from
HO$_2$•CH$_3$C(O)CH$_3$ complexation. These results build on observations reported for lower temperatures where significant CH$_3$C(O)CH$_3$ chaperone enhancement was first observed.$^{30}$

Prior to the improvements to the IRKS system for simultaneous detection of the OH product species described in Section IIa, analogous experiments were independently performed and analyzed in our laboratory that investigated the chaperone effect of CH$_3$C(O)CH$_3$ on the HO$_2$ self-reaction. In that work, only the HO$_2$ and CH$_3$C(O)CH$_2$O$_2$ kinetic traces were observed and analysis was done using FACSIMILE software$^{70}$ (see SI, section SVI). The lack of OH data resulted in the $k_1$ rate constant and $k_{1b}/k_1$ branching fraction parameters being less constrained compared to the results reported in sections IIIa and IIIb. The results of these early experiments are reported here for the first time, also in Figure 10, together with the present data. The CH$_3$C(O)CH$_3$ concentrations from the earlier experiments overlap with those studied here, between 2.1−2.4 × 10$^{16}$ molecule cm$^{-3}$, but also extend to a higher CH$_3$C(O)CH$_3$ (5.2 × 10$^{16}$ molecule cm$^{-3}$). The two sets of data exhibit the same linear dependence of $k_{12,obs}$ with respect to [CH$_3$C(O)CH$_3$]. The agreement between the two datasets taken years apart and analyzed through two independent methods yields a greater confidence in the observed increased HO$_2$ self-reaction rate being due to a chaperone effect. In order to consolidate the earlier datasets which did not account for uncertainties in the overall mechanism rate constants used during the fits, a 4% total uncertainty was used based on the MC fitting analysis (see SVI in SI for more details).

Equation 3 is the result of the combined linear fit, with each dataset weighted by their uncertainties:

$$k_{12,obs} = k_{12} + k''_A [(CH_3)_2CO]_0 = (1.5 \pm 0.1) \times 10^{-12} + (4.0 \pm 0.2) \times 10^{-29} \times [CH_3C(O)CH_3]$$  \ (E3)

where $k''_A = (4.0 \pm 0.2) \times 10^{-29}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ is the chaperone enhancement coefficient for CH$_3$C(O)CH$_3$ at T = 298 K and the intercept, $k_{12}$, agrees with the JPL recommended value.$^{36}$
Figure 10. Experimentally determined values of $k_{12,\text{obs}}$ as a function of CH$_3$C(O)CH$_3$ concentration. The dashed line represents the current recommended value for $k_{12,\text{obs}}$ in the JPL Data Evaluation.\textsuperscript{36} Exp. Data: $k_{12,\text{obs}}$ fits obtained of current data using the Monte Carlo simulations described in Section IIb. Prior Exp. Data: $k_{12,\text{obs}}$ fits of earlier data taken before IRKS modifications fit using FACSIMILE software. The overall fit was weighted by the uncertainties in each value. ($R^2 = 0.9582$).

The magnitude of the chaperone enhancement is dependent on the relative concentration of the H-bonded HO$_2$•CH$_3$C(O)CH$_3$ complex which is determined from the equilibrium constant for the formation of the complex (R15).

$$\text{HO}_2 + \text{CH}_3\text{C(O)CH}_3 \rightleftharpoons \text{HO}_2$\textbullet\text{CH}_3\text{C(O)CH}_3$$ (R15)

The complex enhances the self-reaction rate by R16.

$$\text{HO}_2 + \text{HO}_2$\textbullet\text{CH}_3\text{C(O)CH}_3 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{CH}_3\text{C(O)CH}_3$$ (R16)

The timescale for the attainment of equilibrium for R15 is much faster ($< 100$ $\mu$s) than the millisecond timescale of our kinetic observations. The recommended value$^{36}$ for the equilibrium constant at room temperature, $K_c$(R15) = $(1.4 \pm 0.84) \times 10^{-18}$ cm$^3$ molecule$^{-1}$, is extrapolated from lower temperature studies$^{31, 71}$ with the highest temperature for the $K_c$(R15) measurement being 272 K. $K_c$(R15) at $T = 298$ K can be determined directly here using the method given in Grieman.
et al.\textsuperscript{31} although it is difficult to measure because of the relatively large change in initial [HO$_2$] at $t = 0$ s caused by R4, the reaction of Cl with CH$_3$C(O)CH$_3$ relative to the change caused by the complex equilibrium (R15). (See SVII in SI.) We obtain $K_c(R15) = (2.0 \pm 0.89) \times 10^{-18}$ cm$^3$ molecule$^{-1}$ ($K_{eq}(R15) = 50 \pm 22$, standard state of 1 bar) based on a weighted average of four runs, where the uncertainty includes the propagation of all the estimated experimental errors in addition to the standard deviation from the weighted average. The directly determined value is 40\% higher than the extrapolated recommended value\textsuperscript{36}, but is in agreement. For the CH$_3$C(O)CH$_3$ concentration range shown in Figure 10 for the early datasets ($2.1 - 5.1 \times 10^{16}$ molecules cm$^{-3}$), the percent complexation of HO$_2$•CH$_3$C(O)CH$_3$ ranges between 4.0 – 9.2 \% at room temperature. These results as well as the rate enhancement for the HO$_2$ self-reaction resulting from R15 were incorporated into the MC simulations for determining $k_1$.

The equilibrium constant allows us to estimate the rate constant $k_{16}$ by following the work by Christensen et al. on the HO$_2$ self-reaction CH$_3$OH enhancement.\textsuperscript{67} Under our conditions where $K_c(R15) [(CH_3)_2CO] \ll 1$, and using the constants obtained from Equation 3, we obtain $k_{16}$ from

$$k_{16} = k'^{\infty}_A / K_c(R15) + 2 k_{12} = (2.0 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(E4)

at room temperature, where most of the uncertainty arises from $K_c(R15)$. This value is very similar to the analogous rate constant for the HO$_2$•CH$_3$OH complex which was estimated to be $k_{13} = (2.1 \pm 0.7) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ averaged over $T = 222 – 295$ K at 100 Torr and using a $K_c$ averaged over $T = 230 – 260$ K.\textsuperscript{67} Although there is no determination of the temperature dependence of this rate constant, the magnitude of $k_{16}$ for CH$_3$C(O)CH$_3$ at room temperature is estimated to be the same as that for CH$_3$OH, $k_{14}$, at significantly lower temperatures where the complex formation reactions may be faster at the same pressure.
IIIe. EVALUATION OF OH GENERATION FROM THE CH$_3$C(O)CH$_2$ RADICAL + O$_2$

To assess the potential for OH formation following O$_2$-addition to the CH$_3$C(O)CH$_2$ radical, we studied the unimolecular reaction system outlined in Figure 11 starting from the CH$_3$C(O)CH$_2$ radical (A1) with energetics as shown in Figure S4 (see SI). The reactions include those found to have the lowest barrier heights by Weidman et al.$^{72}$ as well as an additional H-shift following a second O$_2$-addition. The initial reaction is a 1,5 H-shift from the methyl group with an MC-TST calculated rate coefficient of $5.9 \times 10^{-6}$ s$^{-1}$. The high barrier resulting in low rate coefficient for this reaction is in agreement with previous studies$^{17,72-75}$ and has been ascribed to the strain in the TS induced by the sp$^2$-hybridized carbon atom reducing the flexibility.$^{72}$ This means that the 1,5 H-shift is negligible from the thermalized peroxy radical under all relevant time scales and any possible OH-recycling from reactions following this H-shift thus relies on it occurring via excess energy from the O$_2$-addition to the CH$_3$C(O)CH$_2$O$_2$ radical. However, in agreement with most of the previous studies,$^{17,72-74}$ we find that the TS for the 1,5 H-shift is higher in energy than the separated CH$_3$C(O)CH$_2$ radical and O$_2$ (by 3.8 kcal mol$^{-1}$ according to our calculations) and as shown in Figure 12, that means that the H-shift reaction does not occur via excess energy. Thus OH formation based on reactions following this 1,5 H-shift seems a highly unlikely explanation for the observed OH products and currently no explanation has been found for the experimental observations. Very recent high-level results by Weidman et al.$^{72}$ also find that formation of OH is highly unlikely from CH$_3$C(O)CH$_2$ + O$_2$ under ambient conditions. This is in agreement with our calculations which shows that this also applies to our experimental conditions and when considering the possibility of a second O$_2$-addition.
Figure 11. Overview of the reactions modelled using RRKM-ME. Reactions in parentheses are not modelled explicitly, but are assumed to occur with unity yield. MC-TST rate coefficients at 298.15 K calculated using the approach by Møller et al.\textsuperscript{44} are given for the unimolecular reactions and estimated pseudo-first order rate coefficients for the O\textsubscript{2}-additions are given based on the typical experimental conditions of [O\textsubscript{2}] = 1.6 × 10\textsuperscript{18} molecule cm\textsuperscript{3} and k\textsubscript{s} from Table 2.

Figure 12. Time-dependent species population of the modelled system under the experimental conditions. Labels refer to the scheme outlined in Figure 11.
IV. DISCUSSION

This is the first study to measure CH$_3$C(O)CH$_2$O$_2$, HO$_2$, and OH simultaneously to determine the rate constants and branching fractions for the reaction between CH$_3$C(O)CH$_2$O$_2$ and HO$_2$ (R1), and the CH$_3$C(O)CH$_2$O$_2$ self-reaction (R2). As shown in Table 3, prior experimental studies on this system are scarce where the study by Bridier et al (1993)$^{21}$ was the sole paper to measure both rate constants for these reactions. In contrast to their work, the results presented here are not subject to the disadvantage of relying solely on UV absorption techniques, specifically the deconvolution of the UV traces with high uncertainty in the absorption cross-sections. In addition, the chaperone mechanism that we have shown to be substantial was not previously considered. Subsequent work measuring the branching fractions for R1 and R2 through detection of OH relied on the rate constants measured by Bridier et al. (1993) and, therefore, are subject to the same systematic errors. Indeed, the branching fractions reported in the literature for this cross-reaction and self-reaction ranged from 0.15 – 0.67 and 0.50 – 0.75, respectively, indicating that measurements for this system were poorly constrained. By independently re-measuring $\sigma_{\text{CH}_3\text{C(O)CH}_2\text{O}_2}$ in a region where other species absorptions are minimal, characterizing the chaperone effects, and measuring the three species simultaneously, this work is less susceptible to the systematic errors of the previous studies.

<table>
<thead>
<tr>
<th>Ref., year</th>
<th>P (Torr), T (K)</th>
<th>Method</th>
<th>$k_1$</th>
<th>Branching Fractions, $k_1$</th>
<th>$k_2$</th>
<th>Branching Fractions, $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R1a</td>
<td>R1b</td>
<td>R2a</td>
</tr>
<tr>
<td>[25], 1990</td>
<td>760, 298</td>
<td>PR, UVA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.3 (1.6)</td>
</tr>
<tr>
<td>[20], 1993</td>
<td>760, 298</td>
<td>FP, UVA</td>
<td>9.0 (1.0)</td>
<td>-</td>
<td>-</td>
<td>8.0 (2.0)</td>
</tr>
<tr>
<td>[19], 2004</td>
<td>800, 298</td>
<td>FTIR, HPLC, F</td>
<td>-</td>
<td>0.33 (0.13)</td>
<td>0.67 (0.20)</td>
<td>-</td>
</tr>
<tr>
<td>[14], 2008</td>
<td>700, 296</td>
<td>UVP, FTIR</td>
<td>-</td>
<td>-</td>
<td>0.15 (0.08)</td>
<td>-</td>
</tr>
</tbody>
</table>
The rate constants for both the CH$_3$C(O)CH$_2$O$_2$ reaction with HO$_2$ ($k_1$) and the CH$_3$C(O)CH$_2$O$_2$ self-reaction ($k_2$) are both smaller than previously reported by Bridier et al. by about 60%. A possible explanation for this systematic difference is that the UV cross-sections used in the work by Bridier et al. were up to 40 – 60% higher than those determined in this work and those found by other studies.$^{26,29}$ A larger cross-section would result in a larger rate constant. Their method also required that the concentration time dependence of multiple species be de-convoluted from UV spectra, which is susceptible to the uncertainties arising in the absorption cross-sections from all of these species, particularly those arising from secondary chemistry (such as CH$_3$(O)O$_2$, CH$_3$O$_2$, and O$_3$, as shown in the SI). To overcome these challenges, our approach was to accurately re-measure absorption cross-section values for CH$_3$C(O)CH$_2$O$_2$, monitor [CH$_3$C(O)CH$_2$O$_2$] at a wavelength where no other species absorbs, and to simultaneously monitor key species independently using IR-WMS (for which uncertainties are lower) to better constrain the analysis.
An additional reaction mechanism that has not been considered in previous studies involving CH₃C(O)CH₂O₂ is the reaction between CH₃C(O)CH₂O₂ and OH radicals. The reaction between RO₂ and OH reaction has been observed for CH₃O₂, C₂H₅O₂, C₃H₇O₂, and C₄H₉O₂, but there is currently no experimental or theoretical evidence of this reaction for CH₃C(O)CH₂O₂.¹⁰

The potential implications of the OH radical reaction, R17, on the rate parameter values reported in this work have been assessed by adding R17 to the overall reaction mechanism (Table 1).

\[
\text{CH}_3\text{C(O)CH}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{CH}_3\text{C(O)CH}_2\text{O} \quad (\text{R17})
\]

An estimated rate of \((5 \pm 4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and HO₂ product formation was used based on recent work for this class of reactions. The mean value for the rate and branching fraction for R1 were unaffected by the addition of R17 in the MC simulations. However, the uncertainty in \(k_1\) and \(k_{1b} / k_1\) scaled with the input uncertainty for R17. As this was highly subjective, it was not included in the final analysis of this work. Indeed, more work is necessary to understand the reaction rates and product formation channels for this class of reactions and it is beyond the scope of this work.

The branching fractions for the OH formation from R1 determined in this work fall within the large range of values observed previously.¹⁵, ¹⁸⁻²⁰ However, we observe a factor of two more OH formation for this reaction than the IUPAC recommendation.⁶⁵ This is not surprising, because the larger rate constant, \(k_1\), used in previous analyses is directly coupled to the absolute magnitude of the [OH] time dependence. The larger rate constant affects the model by generating OH at relatively faster times where secondary species concentrations that affect the OH loss are smaller. Effectively, a higher observed [OH] would correspond to a smaller branching fraction in the model when using the larger rate constant. Although the branching fraction determined in this work is twice the currently recommended value, it is more consistent with the OH yields
from other peroxy radical + HO$_2$ experiments involving radicals with similar carbon number (e.g. CH$_3$C(O)O$_2$, C$_2$H$_5$(O)O$_2$, C$_3$H$_7$(O)O$_2$, and CH$_3$C(O)CH$_2$O$_2$).$^{36,66,76}$ In comparison to the work by Hasson et al. (2004)$^{20}$, where the branching fraction was observed to be much higher (but also with higher error) than we observe, higher concentrations of CH$_3$C(O)CH$_2$O$_2$ relative to HO$_2$ were used by an average factor of 2. This would make their results more susceptible to uncertainties in the CH$_3$C(O)CH$_2$O$_2$ self-reaction rate parameters which was not reinvestigated in their work.

The branching fraction for the alkoxy formation from the CH$_3$C(O)CH$_2$O$_2$ self-reaction, R$_2$, is lower than that observed by Bridier et al, Emricha and Warneck, and the corresponding IUPAC recommended value which is an average of the two works.$^{21,27,66}$ The work by Bridier et al. deconvoluted overlapping UV kinetic traces as previously discussed and the work by Emricha and Warneck monitored yields of PAN formed after adding NO$_2$ to the system. In the latter, PAN was the only detected species and the yields were expected to be from the reaction of NO$_2$ with CH$_3$C(O)O$_2$ which are formed in the decomposition of CH$_3$C(O)CH$_2$O (R$_2$b). However, NO$_2$ can also react with CH$_3$C(O)CH$_2$O$_2$ to form an organic nitrate, which complicated their analysis. As a result of this complexity, they used their results to provide an upper limit on the branching fraction, which was ultimately lower than the values reported by Bridier et al. The reason for the discrepancy between our results and the literature values is uncertain; however, our direct detection of HO$_2$ and OH is a more constrained tracking of the CH$_3$C(O)CH$_2$O pathway and reduces uncertainties in UV cross-sections and complex side chemistry resulting from nitrate formation.

All experimental data in this work showed evidence for prompt OH formation. This was modeled in the kinetic fits using the CH$_3$C(O)CH$_2$ + O$_2$ reaction (R$_5$b). However, there is
currently no evidence for a mechanism for OH generation from this reaction based on the theoretical work reported here as well as in recent studies.\textsuperscript{17, 72-74} The Cl + HO\textsubscript{2} reaction cannot resolve the discrepancy because prompt OH is observed when investigating the CH\textsubscript{3}C(O)CH\textsubscript{2}O\textsubscript{2} self-reaction. The possibility of contamination in the CH\textsubscript{3}C(O)CH\textsubscript{3} sample was considered. A maximum contamination in the CH\textsubscript{3}C(O)CH\textsubscript{3} sample (0.1\%) with an absorption cross-section of 10\textsuperscript{-18} (\lambda =351 \text{ nm}) under our experimental conditions leading to 100\% OH product would only yield \([\text{OH}] \sim 1 \times 10\textsuperscript{11} \text{ molecule cm}^{-3}\) when photolyzed. In the instance that the maximum potential OH concentration arising from an impurity would be achieved and, it is still not enough to explain our experimental observations which averaged higher prompt OH concentrations. Therefore, the observed prompt OH generation remains unexplained.

Finally, the chaperone effect of CH\textsubscript{3}C(O)CH\textsubscript{3} on the HO\textsubscript{2} self-reaction observed in this work can be compared to a previous study at lower temperatures\textsuperscript{31} as well as to the CH\textsubscript{3}OH chaperone effect which has been studied more extensively.\textsuperscript{67-69} The first observation of the CH\textsubscript{3}C(O)CH\textsubscript{3} chaperone mechanism enhancement was described by Grieman et al.\textsuperscript{31} at significantly lower temperatures and reported a preliminary enhancement coefficient greater than that for CH\textsubscript{3}OH. The work presented here shows the same trend at room temperature under our concentration conditions where the enhancement coefficient due to CH\textsubscript{3}C(O)CH\textsubscript{3} complexation with HO\textsubscript{2} is seen to be approximately three times greater compared to the analogous case with CH\textsubscript{3}OH. In fact, even at room temperature it is easily observable for CH\textsubscript{3}C(O)CH\textsubscript{3}, whereas it is considered negligible for CH\textsubscript{3}OH.

For further comparison, the analogous enhancement coefficient for H\textsubscript{2}O at room temperature is

\[
k''_{\text{H}_2\text{O}} = (0.6 \pm 0.42) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \text{ approximately an order of magnitude smaller than that observed for CH}_3\text{C(O)CH}_3. \text{ The chaperone effect parameters for CH}_3\text{C(O)CH}_3 are}
\]
presented in Table 4 along with those for CH₃OH for comparison. Part of the reason for the
greater enhancement of the HO₂ self-reaction, for CH₃C(O)CH₃ compared to CH₃OH, is the
larger equilibrium constant for the formation of the hydrogen-bonded complex
\( K_c(R15)/K_c(R14) = 2 \). However, the rate constants for the reactions of HO₂ with the respective
hydrogen-bonded complexes appear to be approximately the same, but the temperature
dependence for these values is unknown. More experimental work is needed and an opportunity
for a theoretical explanation is apparent. Regardless, the increased reaction rate for the HO₂ self-
reaction must be considered in laboratory studies of kinetics involving HO₂ in the presence of
significant concentrations of CH₃C(O)CH₃, even at room temperature. At lower temperatures,
particularly those relevant to the tropopause, the chaperone effect has been observed to greatly
increase and needs to be considered in environments containing CH₃C(O)CH₃. We are
currently undertaking a thorough study of the temperature dependence of this effect on HO₂ and
CH₃C(O)CH₂O₂ chemistry. It should also be noted that no acetone concentration dependence
and, therefore, no chaperone dependence was found for the cross-reaction between HO₂ and
CH₃C(O)CH₂O₂ (R1). (See S12 in the SI.)

Table 4. Parameters related to the chaperone effect that enhances the HO₂ self-reaction rate
via the reaction with the H-bonded complexes formed between HO₂ and CH₃C(O)CH₃ (this
work) or CH₃OH. Our values found for CH₃C(O)CH₃ at 298 K are compared to those
previously found for CH₃OH.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HO₂●CH₃C(O)CH₃</th>
<th>Parameter</th>
<th>HO₂●CH₃OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k''_A ) (cm⁸ molecule⁻² s⁻¹)</td>
<td>((4.0 ± 0.2) \times 10^{-29})</td>
<td>( k''_M ) (cm⁸ molecule⁻² s⁻¹)</td>
<td>((1.09 ± 2.7) \times 10^{-29a})</td>
</tr>
<tr>
<td>( K_c(R15) ) (cm³ molecule⁻¹) ( ) (measured)</td>
<td>((2.0 ± 0.89) \times 10^{-18})</td>
<td>( K_c(R14) ) (cm³ molecule⁻¹) ( ) (recommended)</td>
<td>( 1.0 \times 10^{-18c})</td>
</tr>
<tr>
<td>( K_c(R14) ) (cm³ molecule⁻¹) ( ) (recommended)</td>
<td>((1.4 ± 0.84) \times 10^{-18c})</td>
<td>( )</td>
<td>( )</td>
</tr>
</tbody>
</table>
\[
\begin{array}{ccc}
k_{16} \text{ (cm}^3\text{ molecule}^{-1}\text{ s}^{-1}) & (2.0 \pm 1.0) \times 10^{-11} & k_{15} \text{ (cm}^3\text{ molecule}^{-1}\text{ s}^{-1}) & (2.1 \pm 0.7) \times 10^{-11}^{a,d} \\
\text{Range of %} & \text{Range of %} & \\
\text{(H-bonded complex)} & \text{(H-bonded complex)} & \\
[(\text{CH}_3\text{CO}) \text{ (molecule cm}^{-3}\text{)}] & (4.0 - 9.2) & \text{[CH}_3\text{OH} \text{ (molecule cm}^{-3}\text{)}] & (0.36 - 0.70) \\
(2.1 - 5.1) \times 10^{16} & (3.8 - 7.5) \times 10^{15} & \\
\end{array}
\]

\(^a\text{Ref. 67} \quad ^b\text{Ref. 68}; \quad ^c\text{Ref. 35, no uncertainty reported}; \quad ^d\text{Averaged over temperatures < 298 K}

(See text.)

V. CONCLUSIONS

This work measured the rate constants and branching fractions for the reactions between CH$_3$C(O)CH$_2$O$_2$ and HO$_2$, and the associated self-reactions by simultaneously and independently monitoring the time-dependent CH$_3$C(O)CH$_2$O$_2$, HO$_2$, and OH concentrations by UV absorption spectroscopy and infrared 2\textit{f}-heterodyne detection. Kinetic simulations were used to fit the data and determine the uncertainties using a Monte Carlo algorithm. The capacity of this work to monitor three species independently and simultaneously greatly constrains the analysis and gives confidence in the results. Avoiding the need to deconvolve overlapping UV spectra by the use of IR kinetic spectroscopy of individual species results in a more straightforward analysis. The UV cross-sections for CH$_3$C(O)CH$_2$O$_2$ were measured for the spectral region \(\lambda = 290-320\) nm and determined to be higher than the currently recommended values\(^{36}\) but lower than those observed by Bridier et al.\(^{21}\) The CH$_3$C(O)CH$_2$O$_2$ self-reaction rate constant is \((4.8 \pm 0.8) \times 10^{-12}\) molecule$^{-1}$ cm$^3$ s$^{-1}$ and the branching fraction for alkoxy formation inferred from secondary chemistry is \(0.33 \pm 0.13\). The rate constant is lower than the currently recommended values as is the branching fraction. It is not surprising that there is disagreement in the branching fractions considering that the previous studies for the branching fraction were not in agreement with each other and the kinetic rate was not measured in either of the two studies, but was used in their analyses. The cross-reaction between CH$_3$C(O)CH$_2$O$_2$ and HO$_2$ experiments resulted in a rate constant and branching fraction for OH formation of \((5.50 \pm 0.53) \times 10^{-12}\) cm$^3$ molecule$^{-1}$ s$^{-1}$ and
0.30 ± 0.04, respectively. This rate constant is again smaller than the previously reported value whereas the branching fraction is larger. The higher yields of OH observed in this work are more consistent with analogous reactions and ultimately lead to less hydro peroxide product being formed from the reaction between CH₃C(O)CH₂O₂ and HO₂ than previously reported. To fit the experimentally observed OH profiles, a prompt OH formation pathway was necessary, but the mechanism for this remains unclear. The CH₃C(O)CH₃ chaperone effect had a large effect on the rate of the HO₂ self-reaction and was also required to properly fit the experimental results even at room temperature. The chaperone coefficient, $k''_A (T = 298 \text{ K}) = (4.0 \pm 0.2) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, and equilibrium constant, $K_c(R15) = (2.0 \pm 0.89) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$, were determined and should be considered in future peroxy experiments involving HO₂ and CH₃C(O)CH₃.

**ASSOCIATED CONTENT**

**Supporting Information**

The supporting information contains information on the instrumental calibrations, the RRKM-ME modelling, the UV absorption measurements of secondary species, the Facsimile fitting method, determination of the $K_c(15)$ equilibrium constant, and additional chaperone effects.

**ACKNOWLEDGMENTS**

This research was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), supported by the Upper Atmosphere Research and Tropospheric Chemistry Programs. The contribution of K.Z. was supported by the appointment to the NASA Postdoctoral Program at the NASA Jet Propulsion Laboratory, administered by the Universities Space Research Association under contract with NASA. The contribution from A.H. was supported in part by the National Science Foundation (NSF Grant No. CHE-1413712), and the NASA Earth and Science Fellowship (NESSF). M.D.S. was supported by the NASA Earth and Space Science Fellowship (NNX16AO36H). This research was also supported by an appointment of F.J.G. to the NASA Postdoctoral Program at the Jet Propulsion Laboratory, administered by Oak Ridge Associated Universities through a contract with NASA and a SURF grant from Pomona College for E.D. The work by HGK was funded by the Independent Research Fund Denmark. **Author contributions:** S.S. and M.O. conceived and designed the research. K.Z. conducted the experiments and performed the data analysis. F.A.F. assisted with the IRKS instrumental upgrades. C.J.P. helped with experimental planning and the model mechanism. A.O.H., F.J.G., and E.D. conducted the early experiments and F.J.G. performed the data analysis on the part of
that work presented here. M.D.S. wrote the original kinetic analysis library. K.H.M. and H.G.K. contributed the RRKM-ME and MESMER modeling work. K.Z. and F.G. wrote the paper. All authors contributed to the scientific discussion and preparation of the manuscript.

REFERENCES


**TOC Graphic:**

---

ACS Paragon Plus Environment 42