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Time-resolved, broadband UV-absorption spectrometry measurements of Criegee intermediate kinetics using a new photolytic precursor: unimolecular decomposition of CH₂OO and its reaction with formic acid.

The research interests of the group focus on reaction kinetics and oxidation chemistry in gas-phase under low-temperature combustion (autoignition) and atmospheric conditions. This particular work presents experimental and high-level computational kinetic studies of the smallest Criegee intermediate over wide pressure and temperature ranges. Specially, the work presents the group’s new UV-absorption spectrometer, and introduces a new photolytic precursor, CH₂IBr, which photolysis at 213 nm in presence of O₂ produces CH₂OO.

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Time-resolved, broadband UV-absorption spectrometry measurements of Criegee intermediate kinetics using a new photolytic precursor: unimolecular decomposition of CH₂OO and its reaction with formic acid†

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We present a time-resolved broadband cavity-enhanced UV-absorption spectrometer apparatus that we have constructed and utilized for temperature- and pressure-dependent kinetic measurements of formaldehyde oxide (CH₂OO) reactions. We also introduce and utilize a new photolytic precursor, bromoiodomethane (CH₂IBr), which photolysis at 213 nm in presence of O₂ produces CH₂OO. Importantly, this precursor appears to be free from secondary reactions that may regenerate CH₂OO in kinetic experiments. The unimolecular decomposition rate coefficient of CH₂OO has been measured over wide pressure (5–400 Torr) and temperature (296–600 K) ranges and master equation simulations of the decomposition kinetics have been performed using MESMER program. The MESMER simulations of the experimental data with the calculated zero-point energy corrected transition state energy 85.9 kJ mol⁻¹ for decomposition required no adjustment and returned (ΔE)_{down} = 123.2 ± (7298 K)⁰.⁷⁴ cm⁻¹ for temperature-dependent exponential-down model of the collisional energy transfer in He. A very good agreement between results of simulations and experiments is obtained. The results are compared with the previously reported unimolecular decomposition study by Stone et al. (Phys. Chem. Chem. Phys., 2018, 20, 24940–24954). Current master equation simulations suggest about 61% decomposition yield for the predominant H₂ + CO₂ channel, whereas the yields of two other channels, H₂O + CO, and HCO + OH, are sensitive on the parameters involved in the simulations. The kinetics of CH₂OO reaction with formic acid has also been investigated as function of pressure (5–150 Torr) and temperature (296–458 K). The bimolecular rate coefficient for CH₂OO + HCOOH reaction shows a negative temperature dependency, decreasing from (1.0 ± 0.03) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 296 K to (0.47 ± 0.05) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 458 K with an Arrhenius activation energy of –4.9 ± 1.6 kJ mol⁻¹, where statistical uncertainties shown are 2σ. Estimated overall uncertainty in the measured rate coefficients is about ±20%. Current bimolecular rate coefficient at room temperature agrees with the previously reported rate coefficients from the direct kinetic experiments. The reaction is found to be pressure independent over the range between 5 and 150 Torr at 296 K in He.

Introduction

Alkenes are important non-methane hydrocarbon species in the Earth’s atmosphere. Alkenes with natural origin (e.g. isoprene, monoterpenes, and sesquiterpenes) are released into the troposphere from vegetation whereas anthropogenic alkene emissions are often byproducts of combustion and are composed of smaller hydrocarbons (ethene, propenes, butenes, etc.).¹ A major loss pathway of alkenes in the troposphere is reaction with ozone, i.e. ozonolysis. In ozonolysis a highly excited primary ozonide is formed in a very exothermic O₃ + alkene reaction.² In gas phase and at atmospheric pressure, any excited primary ozonide decomposes to a Criegee intermediate, also known as carbonyl oxide, and a carbonyl compound. In case of acyclic (e.g. trans-2-butene, isoprene) and exocyclic (e.g. β-pinene) alkenes, roughly 50% of Criegee intermediates decompose or isomerize further before stabilization, while other ~ 50% are stabilized at atmospheric pressure and are consequently called stabilized Criegee intermediates, sCIs. sCIs can further react with atmospheric constituents (H₂O, (H₂O)₂, SO₂, acids, NO₂, etc.) in bimolecular reactions or decompose and/or isomerize in unimolecular reactions.¹,³
Formaldehyde oxide, CH$_2$OO, is the smallest and probably the most studied scI. It is formed in the ozonolysis of ethene and any larger terminal alkene (e.g. isoprene). In breakthrough experiments using multiplex photoionization mass-spectrometer (MPIMS) utilizing synchrotron radiation for ionization, Welz et al. discovered 2012 that CH$_2$I radical (an $\alpha$-iodoalkyl radical) reaction with molecular oxygen produces the smallest scI, CH$_2$OO.

CH$_2$I + O$_2$ → CH$_2$OO + I \ (R1) \rightarrow \text{other products}

Since high [O$_2$] conditions are easy to prepare, scIs do not react with O$_2$ at any known extent, reaction (R1) is fast and formaldehyde oxide yield is close to unity at low pressures, reaction (R1) is the excellent source of CH$_2$OO for direct kinetic measurements. Impetus to study reaction (R1) with MPIMS originated from this laboratory. Direct kinetics measurements of formaldehyde oxide have shown that CH$_2$OO reacts fast with SO$_2$, organic acids, and water dimer ((H$_2$O)$_2$). Bimolecular rate coefficients of the smallest scI with the above and many other reactants, obtained from direct kinetic measurements in different laboratories, are consistent with each other. For example, results of direct kinetic experiments of CH$_2$OO reaction with SO$_2$ agree with each other and show significantly faster kinetics than now outdated estimates based on results of indirect measurements suggested. Especially CH$_2$OO reactions with acids are very fast with bimolecular rate coefficients in excess of $1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Welz et al. measured a bimolecular rate of $(1.1 \pm 0.1) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction of CH$_2$OO with HCOOH at room temperature ($\sim$ 298 K) and pressure of 4 Torr.

CH$_2$OO + HCOOH → products \ (R2)

Theoretical studies have predicted that the initial reaction step is barrierless (or proceeds through a deep pre-reactive complex), in agreement with the high bimolecular rate coefficient for the reaction at room temperature. However, direct kinetic studies of temperature or pressure dependency of reaction (R2) are not available.

In this work, we measure kinetics of CH$_2$OO + HCOOH reaction over extended temperature (296–458 K) and pressure (5–150 Torr) ranges, report bimolecular rate coefficients, and discuss on the observed kinetics.

Stone et al. have recently measured unimolecular decomposition kinetics of CH$_2$OO in the temperature 450–650 K and helium pressure 2–350 Torr ranges using a time-resolved broadband cavity enhanced absorption spectrometer (TR-BB-CEAS) and probing formaldehyde oxide at UV.

CH$_2$OO → products \ (R3)

The reported rate coefficient for unimolecular decomposition of stabilized CH$_2$OO was $1.1^{+1.5}_{-1.1} \times 10^{-3}$ s$^{-1}$ at atmospheric conditions (298 K and 760 Torr). Even though unimolecular decomposition of stabilized CH$_2$OO is not important reaction under atmospheric conditions, it may play a role under low-temperature-combustion conditions. It has been proposed that CH$_2$OO is an intermediate in combustion of dimethyl ether (DME, CH$_3$OCH$_3$), an important biofuel. In addition, reaction of triplet methylene ($^3$CH$_2$) radical with O$_2$ can produce formaldehyde oxide. Triplet methylene radical is formed, for example, in the combustion of acetylene.

Since the first study by Welz et al. alkyl-substituted $\alpha$-iodoalkyl radicals have also been shown to produce corresponding scIs in presence of oxygen. Hitherto CH$_2$I radical in the reaction (R1) has been prepared by photodissociation of CH$_2$I at 248, 266, or 355 nm. Important for the current work, a reaction between CH$_2$OO and CH$_2$I$_2$ precursor has been observed in many previous studies. This may be a significant problem in kinetic experiments, because only a few percent of the precursor is typically consumed in the photodissociation process and, most importantly, CH$_2$OO + CH$_2$I$_2$ reaction may generate CH$_2$I and thus CH$_2$OO, resulting in chain-propagation and distorting information from kinetic measurements. For example, Liu et al. reported a bimolecular rate coefficient ($5.2 \pm 2.6) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction at 298 K. The reaction becomes faster at higher temperatures. Stone et al. observed a bimolecular rate coefficient $(8.2 \pm 1.7) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 450 K in their unimolecular decomposition study of CH$_2$OO. They also stated that the reaction might have caused a contribution to the measured decay data at the temperatures above 450 K. Buras et al. observed a baseline offset in the 375 nm absorption of CH$_2$OO at high temperatures. They stated that it indicated an extra absorption by an unknown product formed in their system at high temperatures. In addition, CH$_2$I$_2$ has a relatively strong absorption at the 340 nm region, where the typical probing of CH$_2$OO is conducted in UV-absorption-based experiments, leading to a negative (and often non-constant) measurement baseline in most cases.

In this work, we introduce and utilize a new photolytic precursor, bromiodomethane (CH$_3$IBr), which photolysis at 213 nm and in presence of O$_2$ produces CH$_2$OO. This precursor is more stable against secondary reaction chemistry, which may regenerate CH$_2$OO in kinetic experiments. We report a detailed study of thermal unimolecular decomposition kinetics of CH$_2$OO over wide pressure (5–400 Torr) and temperature (296–600 K) ranges using new CH$_3$IBr precursor. We also introduce and utilize our new time-resolved broadband cavity enhanced absorption spectrometer (TR-BB-CEAS) apparatus that locates in the University of Helsinki and probes in the ultraviolet (UV) region. We perform master equation simulations and compare obtained outcome with the current experimental results as well as with the results of unimolecular study by Stone et al.

Experimental

A schematic figure of the new TR-BB-CEAS apparatus utilizing UV absorption to probe CH$_2$OO is shown in Fig. 1. The design of our TR-BB-CEAS apparatus is a modified version of the experimental setup developed by L. Sheps et al. The gas mixture flowing through a quartz tube reactor contained the radical precursor (CH$_3$IBr or CH$_2$I$_2$), O$_2$, and HCOOH (for the bimolecular reaction) diluted...
in helium or nitrogen carrier gas. Calibrated mass flow controllers (Omega Engineering) were used to deliver gases to a mixing manifold before flowing into the reactor. The CH₂I radicals were homogeneously generated along the flow reactor by the 5th harmonic (213 nm) or the 4th harmonic (266 nm) of a pulsed Nd:YAG laser (Quantel Q-smart 850). The photolysis laser beam is expanded by a 2:1 telescope giving an 18 mm diameter spot inside the reactor. Typical pulse fluences at 213 nm and 266 nm were about 4 mJ cm⁻² and 18 mJ cm⁻² inside the reactor, which were sufficient to dissociate approximately 2.5% and 3% of the CH₂IBr and CH₂JI precursors, respectively. The inner diameter of the reactor tube is 36 mm and linear gas flow speed about 1 m s⁻¹, which ensured that the gas mixture was completely replaced between laser pulses with the repetition rate of 1 Hz. The reactor tube is combined with a 2 m long confocal cavity manifold before flowing into the reactor. The CH₂I radicals were principally generated from CH₂IBr by Butler at 210 nm, whereas excitation at 248.5 nm resulted in both C–I bond fission. Based on the CH₂OO absorption signal at 210 nm, whereas excitation at 248.5 nm resulted in selective breaking of the C–Br bond with about 80 m. This region is also free from unwanted interferences of byproducts, e.g. from absorption of IO radical.

The signal from the CMOS line array camera is processed and digitized by a fast 12-bit image acquisition card (National Instruments, PCIe-1427). Single-exponential function \( A_t = A_0 \times \exp(-k't) \) is subsequently fitted to a background-subtracted CH₂OO time-trace by the Levenberg–Marquardt algorithm in a custom-made LabVIEW program. Here \( k' \) is the pseudo-first-order decay rate coefficient, and \( A_0 \) is the absorbance at time \( t \) and \( A_0 \) is the initial absorbance (at time \( t = 0 \)). The wavelength scale of the spectrometer is calibrated with atomic (Hg and Ar) emission lamps. For the experiments described here, we averaged signal between 600 and 3000 shots for each decaying experimental time-trace. Fig. S4 in the ESI† presents a temporal absorption profile of CH₂OO measured at 340 nm with the presence of HCOOH. The estimated initial concentration of CH₂OO was \( \sim 8.5 \times 10^{10} \) molecule cm⁻³ and the observed SNR of the time-trace was \( \sim 35 \) for an averaging time of 1800 s (1800 shots). This yielded a minimum detectable [CH₂OO] of \( \sim 2.4 \times 10^9 \) molecule cm⁻³.

The temperature control of the flow tube reactor is achieved by two temperature-controlled custom-made aluminum blocks, which are placed around the quartz-glass reactor tube. Each aluminum block has four 300 W cartridge heaters, which are regulated using a PID-controller program from LabVIEW. The temperature of the system can be heated anywhere between 296 K and 600 K. Temperature of the gas flow was measured continuously in the middle of the reactor just outside of the photolysis beam by a K-type thermocouple. Complete axial temperature profile within the overlap volume of the probe and the photolysis beams were measured separately for all experimental conditions (temperature, pressure and flow rate) used in this work. The observed temperature uncertainty was ±3 K. The gases were pre-heated close to the setpoint temperature before entering to the reactor.

The CH₂I radicals were principally generated from CH₂IBr at 213 nm.

\[
\text{CH}_2\text{IBr} + h\nu(213 \text{ nm}) \rightarrow \text{CH}_2\text{I} + \text{Br} \quad (R4a)
\]

\[
\rightarrow \text{other products} \quad (R4b)
\]

The UV absorption cross-section of gaseous CH₂IBr as a function of wavelength is presented in Fig. 2. In the photodissociation studies of CH₂IBr by Butler et al., the excitation at 210 nm resulted in selective breaking of the C–Br bond with ~60% yield (Y) as well as concerted IBr elimination (Y < 6%) and simultaneous three-body dissociation to CH₂ + I + Br (≈35%) fragments. No fission of the C–I bond was observed at 210 nm, whereas excitation at 248.5 nm resulted in both C–I and C–Br bond fission. Based on the CH₂OO absorption signal...
observed in our measurements, the photodissociation quantum yield of the C-Br bond at 213 nm is estimated to ~ 0.4 (see ESI†).

A few measurements in this work were done with CH2I2 precursor for comparison.

\[
\text{CH}_2\text{I}_2 + h\nu(266 \text{ nm}) \rightarrow \text{CH}_2\text{I} + \text{I} \quad (\text{R5a})
\]

\[
\rightarrow \text{other products} \quad (\text{R5b})
\]

The absorption cross-section of CH2IBr at 340 nm region (the absorption maximum of CH2OO) is more than 20 times smaller than the cross-section of CH2I2 (see Fig. S2 in the ESI†).33 In kinetic measurement, the stronger absorption of CH2I2 leads typically to a negative (and non-constant) baseline for the measured absorption signal (especially at long delay times). For shorter time scales (<10 ms), the depletion of CH2I2 can be considered as a step function (constant) in time due to photolysis depletion of CH2I2, and it would not affect severely on the kinetic measurement of CH2OO (see Fig. S3 in the ESI†). However, since CH2IBr absorbs much less than CH2I2, our measurements with CH2IBr has a zero or small positive and constant baseline, even with longer measurement time scales (see Fig. S4 in the ESI†).

The thermal unimolecular decomposition of CH2OO is believed to proceed via the formation of a cyclic dioxirane and the transition state leading to its formation determines the rate of reaction from CH2OO to different products. Therefore, accurate estimation of the barrier height and the energy of the cyclic dioxirane is crucial. We performed the T1 diagnostics for the CH2OO reactant, the transition state leading to the formation of the cyclic dioxirane, and the dioxirane intermediate. For the reactant and the TS, the T1 diagnostic has a value of 0.043 and 0.051, respectively, which is an indication of the possibility of multireference character in those systems. Hence, we chose CASSCF method to carry out the electronic structure calculations. All above methods have been implemented in Gaussian 16 suite of programs.38

In order to get reliable energies, we performed single-point energy calculations with domain based local pair natural orbital coupled cluster methods or the DLPNO-CCSD(T) approach as employed in ORCA code.39 The DLPNO calculations were then extrapolated to the complete basis set limit using correlation consistent Dunning’s augmented basis sets, i.e., aug-cc-pVXZ (X = 5 and 6)40,41 following the extrapolation scheme as given below42

\[
\Delta E_{\text{CBS}} = \Delta E_{\text{aug-cc-pVXZ}} - 0.694(\Delta E_{\text{aug-cc-pV5Z}} - \Delta E_{\text{aug-cc-pV6Z}})
\]

where \(\Delta E\)s are the energies relative to the reactant.

To account for the effect of helium bath-gas pressure on unimolecular decomposition rate coefficient of CH2OO, we performed master equation simulations using MESMER 5.1 [Master Equation Solver for Multi-Energy well Reactions] program.43 For well-defined transition states Rice–Ramsperger–Kassel–Marcus (RRKM) theory was used along with Eckart tunneling corrections to calculate microcanonical rate coefficients. For collisional energy transfer a temperature-dependent single-exponential-down model was used.

\[
\langle \Delta E \rangle_{\text{down}} = \langle \Delta E \rangle_{\text{down,ref}}(T/298 \text{ K})^n
\]

Here, \(\langle \Delta E \rangle_{\text{down,ref}}\) is collision energy transfer parameter at 298 K and its temperature dependency is governed by \(n\). The terms \(\langle \Delta E \rangle_{\text{down,296K}}\) and \(n\) were used as fitting parameters in the master equation simulations to best agree with experimental data by minimizing \(\chi^2\), i.e. principally minimizing difference of calculated and experimental unimolecular decomposition rate coefficients. MESMER uses Lennard-Jones model for calculating the collisional frequency and requires the depth of the potential well, \(\varepsilon_{IJ}\) and the finite length where the potential is zero, \(\sigma_{IJ}\).

### Results and discussion

#### CH2OO spectrum

The absorption spectrum of CH2OO measured in this work, produced using the CH2IBr precursor and 213 nm photolysis followed by reaction (R1), is shown with blue line in Fig. 3. The spectrum is averaged over 0–3 ms (with ~67 μs time resolution) after the photolysis. The corresponding transient spectrum is

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**Theoretical methods**

In this work we accompanied the same potential energy surface (PES) for the thermal unimolecular decomposition of the smallest Criegee intermediate, CH2OO, as Stone et al.9 utilized in their study. Their PES was to significant extent based on Nguyen et al. calculations.36 The geometry optimization along with the vibrational frequency calculations of the stationary points on the PES, viz., CH2OO, transition states, and intermediates were performed using complete active space self-consistent field (CASSCF) method taking into account 8 electron and 8 orbital combination in the active space, i.e., CASSCF(8,8). The products and one transition state leading to the formation of H2O + CO, were optimized with MN1537 density functional. In all these cases, def2-TZVP basis set was used.

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**Fig. 2** The UV absorption cross-section of gaseous CH2IBr as a function of wavelength.33
The absorption cross-section is estimated using the measured absorption coefficient at $t = 0$ ms, and the resulting initial CH$_2$I concentration using the estimated yield of the channel (R4a) = 0.4. The estimated initial CH$_2$OO concentration in the measurement is $\sim 2.0 \times 10^{11}$ molecule cm$^{-3}$. The O$_2$ concentration was $\sim 3.8 \times 10^{19}$ molecule cm$^{-3}$.

**Bimolecular CH$_2$OO + HCOOH reaction**

The kinetics of CH$_2$OO reaction with formic acid was measured as a function of temperature between 296 and 458 K at low pressure (5–15.5 Torr). Fig. 4 shows typical transient traces of CH$_2$OO at varying concentrations of HCOOH at 458 K. All the CH$_2$OO traces were fitted using a single-exponential decay function. In the absence of added acid reactant, the CH$_2$OO signal follows a first-order decay loss, $k_{\text{loss}}$ (s$^{-1}$), which originates from diffusion out of the measurement volume, from slow reaction of CH$_2$OO with the precursor, and to some small extend from radical–radical reactions. Heterogeneous loss is negligible in our measurement system, since the radicals are generated and probed inside the same volume element in the middle of the flow reactor tube away from wall. In addition, the measurements were done in a temperature region where the unimolecular decomposition is negligible (below 475 K). The $k_{\text{loss}}$ was measured by reducing the precursor concentration until its value no longer depended on the precursor concentration. Once this condition was obtained, it was concluded that radical–radical reactions, especially CH$_2$OO–CH$_2$OO reactions, were suppressed. The initial CH$_2$OO concentration in the measurements was typically below $1.0 \times 10^{11}$ molecule cm$^{-3}$, which was estimated from the laser fluence, the precursor absorption cross-section$^{33}$ and the effective OPL at the used wavelength (see ESI† for more details).

By adding acid, the decay of CH$_2$OO became faster. All the measurements were performed under pseudo-first-order conditions, i.e. [CH$_2$OO] $\ll$ [HCOOH]. The photolysis of formic acid, HCOOH + $h\nu$(213 nm) → HCO + OH, was negligible ($\sim 0.06\%$) in our measurements, because of low laser fluence ($\sim 4$ mJ cm$^{-2}$) and small absorption cross-section of HCOOH at 213 nm (1.4 $\times$ $10^{-19}$ cm$^2$ molecule$^{-1}$). Even at the highest [HCOOH] used, 2.06 $\times$ $10^{13}$ molecule cm$^{-3}$, the resulting [OH] was only about 1.0 $\times$ $10^{10}$ molecule cm$^{-3}$, which could not have any important effect on the current measurements. Concomitant product of photolysis, HCO radical, would rapidly react with O$_2$ and form HO$_2$ radical that, due to its low reactivity, would have even smaller effect than the OH radical. In Fig. 5, the obtained pseudo-first-order decay rate coefficients ($k_{\text{obs}}$) of CH$_2$OO are shown as function of temperature and [HCOOH]. The bimolecular...
rate coefficient $k(\text{CH}_2\text{OO} + \text{HCOOH})$ is obtained from the slope of the equation $k_{\text{obs}} = k_{\text{loss}} + k(\text{CH}_2\text{OO} + \text{HCOOH}) \times [\text{HCOOH}]$ fitted to the data, while the intercept reflects the $k_{\text{loss}}$. Obtained bimolecular rate coefficients were measured with both precursor-photoysis wavelength combinations and the results are shown in Table 1 along with experimental conditions and statistical 2σ experimental uncertainties. Estimated overall uncertainties in the measured rate coefficients are about ±20%. The current bimolecular rate coefficient $(1.0 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for CH$_2$OO + HCOOH reaction measured at room temperature agrees with the previously reported rate coefficients $(1.1 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured by Welz et al.$^{15}$

Theoretical studies suggest that CH$_2$OO + HCOOH reaction proceeds through a barrierless addition of the reactants leading to hydroperoxymethylformate (HPMF).$^{18,19}$ In study by Vereecken,$^{19}$ the rate coefficient $(1.0 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is predicted at room temperature with very minor negative temperature dependency (~8%) between 250 and 350 K. Current bimolecular rate coefficient at 458 K is about factor of two slower than the rate coefficient at room temperature, giving negative temperature dependency ~50%. Fig. 6 shows an Arrhenius plot of the measured bimolecular rate coefficients of CH$_2$OO + HCOOH reaction. The least squares fit to the data gives an Arrhenius expression, $k = (1.5 \pm 0.8) \times 10^{-11} \exp[-4.9 \pm 1.6] \text{ KJ mol}^{-1}/\text{RT}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with 2σ standard fitting uncertainties.

The bimolecular rate coefficient of the reaction was measured also as a function of helium density at 296 K. Fig. 7 presents the obtained pseudo-first-order decay rate coefficients ($k_{\text{obs}}$) of CH$_2$OO as function of pressure and [HCOOH]. A complete set of the results and experimental conditions is shown in Table S1 (in the ESI†). The reaction appears to be pressure independent over the range between 5 and 150 Torr, especially once considering the uncertainty of the measurements. An increase in the baseline of the measured absorption signal was observed at high pressures (with added HCOOH), which is possibly due to an enhanced stabilization of ICH$_2$OO at higher pressure (see more details in the ESI†).

For comparison, the temperature dependency of the reaction was also measured using diiodomethane (CH$_2$I$_2$) precursor with 266 nm photolysis. The results are given in Table 1, which show that outcome of both precursor-photoysis wavelength combinations are in agreement with each other. The obtained Arrhenius expression for the CH$_2$I$_2$ study was $k = (1.1 \pm 0.4) \times 10^{-11} \exp[-5.9 \pm 0.8] \text{ KJ mol}^{-1}/\text{RT}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with 2σ standard fitting uncertainties. The inert buffer-gas in the measurements was nitrogen (N$_2$).
Unimolecular decomposition of CH₂OO

**Experiments.** All the transient absorption traces of CH₂OO were measured at 338 nm and fitted to first-order, single-exponential decay function shown above. The obtained thermal unimolecular decomposition rate coefficients of CH₂OO are shown in Fig. 8 as function of temperature and helium buffer-gas pressure, whereas the complete kinetic results with conditions are shown in Table 2. The initial CH₂OO concentration used in the measurements was below $2.0 \times 10^{11}$ molecule cm$^{-3}$, which efficiently suppressed radical–radical, especially CH₂OO–CH₂OO, reactions. Experiments were also performed with higher precursor concentration, but with lower laser fluence, to test a possible importance of Criegee-precursor, CH₂OO + CH₂IBr reaction. The measured unimolecular decay rate coefficients are shown in Fig. 9 as function of [CH₂IBr] at various temperature and pressure conditions. Even at 575 K, the measured unimolecular decay rate coefficients do not depend on the [CH₂IBr] to any significant extent. One potentially very important advantage of the new photolytic precursor is that it is more stable against secondary/surface chemistry since it does not produce CH₃I radical (and consequently CH₂OO) in $X + CH₂IBr \rightarrow XI + CH₂Br$ reaction, where $X$ is any species.

The unimolecular reaction rate coefficient $k_{\text{uni}}$ at given temperature and total density is obtained by $k_{\text{uni}} = k_{\text{obs}} - k_{\text{loss}}$, where both $k_{\text{obs}}$ and $k_{\text{loss}}$ are measured decay rate coefficients from single-exponential function fits to the experimental traces. The $k_{\text{loss}}$ is measured at a few temperatures below which any significant unimolecular decomposition reaction occurs, whereas the $k_{\text{obs}}$ is measured at a temperature where significant unimolecular reaction occurs, i.e., $k_{\text{obs}} > 3k_{\text{loss}}$. At low pressures ($p < 20$ Torr), the $k_{\text{loss}}$ depends strongly on total density, decreasing from $\sim 100$ s$^{-1}$ at low total density to $\sim 20$ s$^{-1}$ at high total density. However, values of $k_{\text{loss}}$ at each total density stay almost constant between the temperatures 296 K and 375 K, which is reasonable, since diffusion has a weak temperature dependency. The unimolecular decomposition reaction starts to become significant at temperatures only at and above 425 K (see Fig. S9 in the ESI†). Thus, mean of the measurements performed between 296 and 375 K was used as the $k_{\text{obs}}$.

A positive baseline offset of the measured absorption signal was also present at high pressures in the thermal unimolecular decomposition measurements. The offset value increased as pressure increased indicating the possible enhanced stabilization of ICH₂OO as observed in the bimolecular CH₂OO + HCOOH reaction. However, in constant (high) density, the baseline offset decreased as the temperature increased indicating a possible decomposition of ICH₂OO. Interestingly, at high temperatures, a small offset was present already at low pressures, which might indicate possible absorption by another formed product than ICH₂OO. The baseline offset has been taken into account in the fitting of the first-order, single-exponential decays (see more details in ESI†).

The unimolecular decomposition rate coefficient data shown in Fig. 8 were fitted simultaneously (a global fit) using the following Troe expression
t employing the nonlinear least squares fitting method

$$k_{\text{obs}}(|M|, T) = \frac{k_0(T)|M|}{1 + \frac{k_0(T)|M|}{k_{\infty}(T)}} \times F_c^p, \quad (3)$$

where $k_0(T)$ is the limiting low-pressure rate coefficient for CH₂OO decomposition, $k_{\infty}(T)$ is the limiting high-pressure rate coefficient for CH₂OO decomposition, $M$ is the total number density, $F_c$ is the broadening factor, and the exponent $p$ is given by

$$p = \left(1 + \frac{\log_{10}\left(\frac{k_0(T)|M|}{k_{\infty}(T)}\right)}{N}\right)^{-1}, \quad (4)$$

where $N = 0.5 - 1.27 \log_{10}F_c$ is the width parameter. The global fits using eqn (3) were performed with $F_c$ and $N$ fixed to values of 0.64 and 1.0, respectively, or $F_c$ allowed to float independently at each temperature. The fits with fixed $F_c$ and $N$ values gave lower $\chi^2$-value, although the parameterisations from each fit were in
Table 2 Unimolecular decomposition kinetics (rate coefficients) of CH$_2$OO determined from the UV experiments. $k_{uni}$ are the fitted single-exponential decay rate coefficients of CH$_2$OO, with 2σ statistical fitting uncertainties. $k_{uni}$, are derived as $k_{uni} = k_{uni} - k_{loss}$. Troe fits to $k_{uni,Troe}$, $k_{uni,MESMER}$ are derived using eqn (3). $k_{uni,MESMER}$ are the results of MESMER simulations. Unimolecular data shown in italics (at 425 K) were not included in the MESMER fits. The stated MESMER values at 425 K were calculated using the resulted MESMER fit parameters. The unimolecular data shown in italics (at 575 and 600 K) were also not included in the Troe fits. The stated Troe values were calculated using the resulted Troe fit parameters. High pressure limiting rate coefficients ($p = \infty$) are taken from MESMER simulations at $p = 10$ atm.

Table 2 (continued)

| $T$ (K) | [He] ($\times 10^{18}$ molecule cm$^{-2}$) | $p^0$ (Torr) | $k_{obs}$ (s$^{-1}$) | $k_{uni}$ (s$^{-1}$) | $k_{uni,Troe}$ (s$^{-1}$) | $k_{uni,MESMER}$ (s$^{-1}$) |
|--------|---------------------------------------|--------------|-----------------|-----------------|-----------------|-----------------|
| 525.0  | 8.9                                  | 475 $\pm$ 29 | 100              | 375             | 344             | 306             |
| 550.0  | 9.3                                  | 767 $\pm$ 58 | 100              | 667             | 706             | 606             |
| 575.0  | 9.75                                | 1319 $\pm$ 119 | 100              | 1229            | 1359            | 1123            |
| 600.0  | 10.15                                | 2170 $\pm$ 351 | 100              | 2070            | 2473            | 1956            |
| 625.0  | 10.5                                  | 3093 $\pm$ 610 | 100              | 3031            | 4473            | 3318            |

$^a$ The fixed O$_2$ concentration was $\sim 3.9 \times 10^{18}$ molecule cm$^{-2}$.

Fig. 9 Measured unimolecular decomposition rate coefficients of CH$_2$OO as function of CH$_2$Br concentration in different temperature and total density conditions. The statistical uncertainties shown are 2σ.

agreement within the fitting uncertainties. The fit with fixed $F_c$ and $N$ values gives $k_b(T) = (1.3 \pm 3.0) \times 10^{-8} \exp[-8065 \pm 1170/(T)]$ cm$^3$ mol$^{-1}$ s$^{-1}$ and $k_c(T) = (7.8 \pm 17.8) \times 10^{11} \exp[-9716 \pm 1088/(T)]$ s$^{-1}$, where statistical uncertainties stated are 2σ.

Master equation analysis. The PES for the unimolecular decomposition reaction of CH$_2$OO used in master equation simulations is plotted in Fig. 10. The energies are given in kJ mol$^{-1}$ and the naming of the species involved in the decomposition path were kept the same as that reported by Stone et al.$^8$ for comparison. The energetics in the present work are quite similar to those obtained by Nguyen et al.$^{38}$ and Stone et al.$^8$ the differences originating from the use of different electronic structure theories.
There are few notable exceptions that were observed in this work. The first one is the energy values obtained for TS6 and TS6a. While the present work suggests almost negligible difference between energies of these two species, previous works indicates a difference of about 16 kJ mol\(^{-1}\). This difference, however, does not affect the product yields for different channels. The second one is related to the TS2 in Fig. 10, which has a non-superimposable mirror image and hence we set the transition state optical isomer value to 2 in MESMER. Since no LJ parameters are available for the CH\(_2\)OO, we approximated them using the corresponding values of HCOOH, for which \(\sigma = 3.79\) Å and \(\epsilon = 520\) K.\(^{49,50}\) Fitting of the \(\langle \Delta E \rangle\)\(_{\text{down},298K}\) and \(n\) parameters to the experimental rate coefficient data was done using Levenberg–Marquardt algorithm as implemented in MESMER, resulting the following relation for the collisional energy transfer expression

\[
\langle \Delta E \rangle_{\text{down}} = 123.2 \times (T/298\ \text{K})^{0.74},
\]

where, \(\langle \Delta E \rangle_{\text{down},298K} = 123.2\) cm\(^{-1}\) and the temperature dependency parameter \(n = 0.74\). As the use of single-exponential-down model in master equation simulations has been extensive in literature, a set of \(\langle \Delta E \rangle_{\text{down}}\) values has emerged. In the present work, both collisional energy transfer parameters obtained from fitting are within the expected range of values at room temperature.\(^{13}\) Interestingly, combination of DLPNO-CCSD(T)/CBS(aug-cc-pV5Z, aug-cc-pV6Z)/CASSCF(8,8)/def2-TZVP energies calculated in this work with the fitted parameters provide such an excellent agreement with the experimental rate coefficient data of CH\(_2\)OO unimolecular decomposition that we do not need to tune the energies of neither the barrier nor the intermediate dioxirane. This further exemplifies the accuracy of our theoretical calculations as well as coherence between theory and experiments. The master equation results are in very good agreement with the experimental rate coefficients and justifies the high-pressure limiting values (\(p = 10\) atm) presented in Table 2.

In literature several values are reported for the decomposition barrier of CH\(_2\)OO to cyc-H\(_2\)COO, ranging from 76 to 100 kJ mol\(^{-1}\).\(^{49}\) Our calculated barrier 85.92 kJ mol\(^{-1}\) lies well within this range. To further test compatibility between the current computational and experimental results, we performed MESMER simulations by fitting simultaneously not only the collisional energy transfer parameters but also the barrier height so as to observe any change in the barrier height. We noticed that using Eckart tunneling, the decomposition barrier increases slightly by 1.6 kJ mol\(^{-1}\), when fitting all three parameters simultaneously. On the other hand, when no tunneling is used, the barrier goes down by 1.8 kJ mol\(^{-1}\). A comparison between the current MESMER simulation and the simulations with floating all three parameters is provided in Fig. S10 of the ESI\(^{\dagger}\) along with the experimental rate coefficients.

Product yields for the three different channels, \(\nuiz.,\) H\(_2\) + CO\(_2\), H\(_2\)O + CO, and HCO + OH presented in Fig. 10 were also estimated. According to MESMER simulations, H\(_2\) + CO\(_2\) is the predominant channel with 60.8% yield, whereas yields of the other two channels, H\(_2\)O + CO, and HCO + OH, can differ depending on the parameters involved in the simulations. The formation of HCO + OH is believed to proceed \(\text{via}\) irreversible decomposition of t-H\((\text{C(O)}\)OH without a clear transition state. Hence, in the present work, we have used a measured value \(k(\text{HCO + OH}) = 1.83 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), as reported by Temps \textit{et al.}\(^{51}\) for the pre-exponential factor in the modified Arrhenius expression, without any temperature dependency, to obtain the yield of the OH-radical formation channel. Our results indicate the formation of H\(_2\)O + CO channel with an

**Fig. 10** Zero-point inclusive potential energy surface (PES) for the unimolecular decomposition of CH\(_2\)OO in kJ mol\(^{-1}\). The names of the species involved in the PES were taken from the works of Stone \textit{et al.}\(^9\) and Nguyen \textit{et al.}\(^{36}\) The portion of the PES used in MESMER calculations to fit the experimental rate coefficient data is shown in pink along with the structure of the crucial transition state.
overall yield of 30.9%, while the least dominant OH + HCO channel was having a percentage yield of 8.3.

In order to facilitate the utilization of current MESMER results in combustion or atmospheric chemistry models, we provide modified Arrhenius representations in ChemKin PLOG format (see ESL†) for the PES illustrated in Fig. 10. Also a MESMER input file is given in ESL†

Comparison with the previous measurements. In Fig. 11, we compare the current results (filled circles and solid lines) with those of Stone et al., previous work (hollow triangles). The hollow triangles with the corresponding error bars are part of the experimental rate coefficient data that Stone et al. included in their MESMER fits at temperatures from 500 to 600 K (the fits included also data from 650 K). Due to the substantial background losses in their measurements, some of the low-pressure data at 500, 525, and 550 K, and all the data from the lowest two temperatures (450 and 475 K) were left out of their MESMER fittings. Since in the current measurements the background losses, \( k_{\text{obs}} \), were generally much smaller than the observed decay rates (see Table 2), \( k_{\text{obs}} \), we could fit all our unimolecular data in the master equation simulations (excluding the data from 425 K).

The reported unimolecular decomposition rate coefficients of Stone et al. are more than two times smaller than our values at all temperatures shown in Fig. 11. Overall, their values are about 20–40% of our values with an average of 25%. This appreciable difference could be due to the reaction CH\(_2\)OO + CH\(_2\)I\(_2\), which might have caused, as they also state, a contribution to their measured decay rate coefficient data at the temperatures above 450 K. Differences are also observed in the fitted energy-transfer parameters of the MESMER simulations. While simulations of the current work produce 123.2 cm\(^{-1}\) and 0.74 values for the collisional energy transfer parameters \( \Delta E_{\text{down},298K} \) and \( n_i \) respectively, Stone et al. report corresponding values of 32.6 cm\(^{-1}\) and 1.7 for the thermal unimolecular decomposition of CH\(_2\)OO.

Conclusions

In this work we have presented a new TR-BB-CEAS apparatus for kinetic studies of reactive intermediates, which are probed utilizing their UV-absorption. We show the capability of and use the new set-up for temperature- and pressure-dependent measurements of formaldehyde oxide (CH\(_2\)OO) reactions. The spectrometer is able to simultaneously measure transient absorption spectra over the wavelength range 300–450 nm with the time resolution of 50 μs using a fast CMOS line array camera-based grating spectrometer. The line array camera enables the transient spectra to be measured without any moving parts inside the grating spectrometer. For CH\(_2\)OO, we could reach a detection limit \( \sim 2.4 \times 10^9 \) molecule cm\(^{-3}\) at 340 nm region with an averaging time of 30 min. This work also reveals a new photolytic precursor for formaldehyde oxide, bromoiiodomethane (CH\(_2\)I\(_2\)), which photolysis at 213 nm in presence of O\(_2\) produces CH\(_2\)OO. This new precursor was found to be free from secondary reactions that may regenerate CH\(_2\)OO in kinetic experiments. In addition, depletion of CH\(_2\)I\(_2\) in a photolysis does not produce a negative baseline shift for the CH\(_2\)OO absorption trace signal because of much smaller absorption cross-section of bromoiiodomethane at 340 nm region.

The bimolecular rate coefficient for CH\(_2\)OO + HCOOH reaction was found to have a negative temperature dependency, decreasing from \( (1.0 \pm 0.03) \times 10^{-10} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 296 K to \( (0.47 \pm 0.05) \times 10^{-10} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 458 K with an Arrhenius activation energy \( \sim 4.9 \pm 1.6 \) kJ mol\(^{-1}\). The obtained bimolecular rate coefficient at room temperature agrees with the previously reported rate coefficients from the direct kinetic experiments by Welz et al.\(^{15}\) Photodissociation of HCOOH reactant was found to be negligible and, consequently, did not have any important effect on the bimolecular kinetics of the CH\(_2\)OO + HCOOH reaction. However, if a reactant absorbs strongly at 213 nm, its photolysis could be a problem in bimolecular reaction kinetic measurements. This may well be the case with SO\(_2\) reactant, which absorbs radiation strongly at 213 nm.\(^{22}\) In the current study, the CH\(_2\)OO + HCOOH reaction was also found to be pressure independent over the range between 5 and 150 Torr of helium at 296 K.

Our kinetic measurements of thermal unimolecular decomposition of CH\(_2\)OO over wide pressure (5–400 Torr) and temperature (296–600 K) ranges confirm the previously results that...
the thermal unimolecular decomposition is not an important atmospheric sink of CH$_2$OO$^{9,53}$ and the decomposition only becomes significant at temperatures above 425 K. Due to this reason, thermal unimolecular decomposition of CH$_2$OO might play an important role under low-temperature combustion conditions.

A very good agreement between the experimental results and master equation simulations performed using MESMER code was obtained by fitting collision energy transfer parameters to the experimental data without tuning any transition state energy. This evidences high coherence between experiments and theory. The MESMER simulations suggest 60.8% decomposition yield for the predominant H$_2$ + CO$_2$ channel. Yields of two other channels, H$_2$O + CO, and HCO + OH, are sensitive on the parameters involved in the simulations. Constraining simulations with an experimental value for (reverse) HCO + OH reaction, simulations return 30.9% and 8.3% yields for H$_2$O + CO and HCO + OH reaction channels, respectively.

Appreciable differences observed between the current experimental thermal unimolecular decomposition kinetics of CH$_2$OO and the results of Stone et al.$^9$ measurements are suggested to originate from the use of different photolytic precursors.

Conflicts of interest
Authors declare no conflicts of interest.

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References
1 L. Vereecken, A. Novelli and D. Taraborrelli, Phys. Chem. Chem. Phys., 2017, 19, 31599–31612.
2 R. Criegee, Angew. Chem., Int. Ed. Engl., 1975, 14, 745–752.
3 M. A. H. Khan, C. J. Percival, R. L. Caravan, C. A. Taatjes and D. E. Shallercross, Environ. Sci.: Processes Impacts, 2018, 20, 437–453.
4 C. A. Taatjes, G. Meloni, T. M. Selby, A. J. Trevitt, D. L. Osborn, C. J. Percival and D. E. Shallercross, J. Am. Chem. Soc., 2008, 130, 11883–11885.
5 O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallercross and C. A. Taatjes, Science, 2012, 335, 204–207.
6 Y. Su, Y. Huang, H. A. Witek and Y. Lee, Science, 2013, 340, 174–176.
7 L. Sheps, J. Phys. Chem. Lett., 2013, 4, 4201–4205.
8 W. Chao, J. Hsieh, C. Chang and J. J. M. Lin, Science, 2015, 347, 751–754.
9 D. Stone, K. Au, S. Sime, D. J. Medeiros, M. Blitz, P. W. Seakins, Z. Decker and L. Sheps, Phys. Chem. Chem. Phys., 2018, 20, 24940–24954.
10 D. Johnson and G. Marston, Chem. Soc. Rev., 2008, 37, 699–716.
11 A. J. Eskola, D. Wojcik-Pastuszka, E. Ratajczak and R. S. Timonen, Phys. Chem. Chem. Phys., 2006, 8, 1416–1424.
12 H. Huang, A. J. Eskola and C. A. Taatjes, J. Phys. Chem. Lett., 2012, 3, 3399–3403.
13 H. Huang, B. Rotavera, A. J. Eskola and C. A. Taatjes, J. Phys. Chem. Lett., 2013, 4, 3824.
14 J. L. Miller, Phys. Today, 2012, 65, 17–19.
15 O. Welz, A. J. Eskola, L. Sheps, B. Rotavera, J. D. Savee, A. M. Scheer, D. L. Osborn, D. Lowe, A. Murray Booth, P. Xiao, M. A. H. Khan, C. J. Percival, D. E. Shallercross and C. A. Taatjes, Angew. Chem., Int. Ed., 2014, 53, 4547–4550.
16 J. J. M. Lin and W. Chao, Chem. Soc. Rev., 2017, 46, 7483–7497.
17 R. Chhintyal-Pun, A.Davey, D. E. Shallercross, C. J. Percival and A. J. Orr-Ewing, Phys. Chem. Chem. Phys., 2015, 17, 3617–3626.
18 B. Long, J. Cheng, X. Tan and W. Zhang, THEOCHEM, 2009, 916, 159–167.
19 L. Vereecken, Phys. Chem. Chem. Phys., 2017, 19, 28630–28640.
20 A. Andersen and E. A. Carter, J. Phys. Chem. A, 2003, 107, 9463–9478.
21 A. Andersen and E. A. Carter, Mol. Phys., 2008, 106, 367–396.
22 B. Z. Chen, J. M. Anglada, M.-B. Huang and F. Kong, J. Phys. Chem. A, 2002, 106, 1877–1884.
23 R. A. Alvarez and C. B. Moore, J. Phys. Chem., 1994, 98, 174–183.
24 J. M. Beames, F. Liu, L. Lu and M. I. Lester, J. Chem. Phys., 2013, 138, 20045.
25 C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallercross, B. Rotavera, E. P. Lee, J. M. Dyke, D. K. Mok, D. L. Osborn and C. J. Percival, Science, 2013, 340, 177–180.
26 Y. Chang, C. Chang and K. Takahashi, Chem. Phys. Lett., 2016, 653, 155–160.
27 F. Liu, J. M. Beames, A. M. Green and M. I. Lester, J. Phys. Chem. A, 2014, 118, 2298–2306.
28 D. Stone, M. Blitz, L. Daubney, N. U. M. Howes and P. Seakins, Phys. Chem. Chem. Phys., 2014, 16, 1139–1149.
29 Y. Liu, F. Liu, S. Liu, D. Dai, W. Dong and X. Yang, Phys. Chem. Chem. Phys., 2017, 19, 20786–20794.
30 Z. J. Buras, R. M. Elsamra, A. Jalan, J. E. Middaugh and W. H. Green, J. Phys. Chem. A, 2014, 118, 1997–2006.
31 L. Sheps and D. W. Chandler, Time-Resolved Broadband Cavity-Enhanced Absorption Spectroscopy for Chemical Kinetics, Sandia National Laboratories, Livermore, CA, 2013, SAND2013–2664.
32 J. J. Scherer, J. B. Paul, H. Jiao and A. O'Keefe, Appl. Opt., 2001, 40, 6725–6732.
33 J. C. Mo¨ssinger, D. E. Shallercross and R. A. Cox, J. Chem. Soc., Faraday Trans., 1998, 94, 1391–1396.
34 L. Butler, E. Hintsa and Y. Lee, J. Chem. Phys., 1986, 84, 4104–4106.
35 L. Butler, E. Hintsa, S. F. Shane and Y. Lee, J. Chem. Phys., 1987, 86, 2051–2074.
36 T. Nguyen, R. Putikam and M. C. Lin, J. Chem. Phys., 2015, 142, 124312.
37 H. S. Yu, X. He, S. L. Li and D. G. Truhlar, Chem. Sci., 2016, 7, 5032–5051.
38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford, CT, 2016.
39 F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2018, 8, e1327.
40 A. K. Wilson, T. van Mourik and T. H. Dunning, THEOCHEM, 1996, 388, 339–349.
41 K. A. Peterson, D. E. Woon and T. H. Dunning, J. Chem. Phys., 1994, 100, 7410–7415.
42 T. T. Pekkanen, R. S. Timonen, G. Lendvay, M. P. Rissanen and A. J. Eskola, Proc. Combust. Inst., 2019, 37, 299–306.
43 D. R. Glowacki, C. Liang, C. Morley, M. J. Pilling and S. H. Robertson, J. Phys. Chem. A, 2012, 116, 9545–9560.
44 W. Ting, Y. Chen, W. Chao and M. C. Smith, Phys. Chem. Chem. Phys., 2014, 16, 10438–10443.
45 A. Winkler and P. Hess, J. Am. Chem. Soc., 1994, 116, 9233–9240.
46 D. Singleton, G. Paraskevopoulos and R. Irwin, J. Photochem., 1987, 37, 209–216.
47 J. Troe, J. Phys. Chem., 1979, 83, 114–126.
48 V. P. Barber, S. Pandit, A. M. Green, N. Trongsiriwat, P. J. Walsh, S. J. Klippenstein and M. I. Lester, J. Am. Chem. Soc., 2018, 140, 10866–10880.
49 T. Berndt, R. Kaethner, J. Voigtländer, F. Stratmann, M. Pfeifle, P. Reichle, M. Sipilä, M. Kulmala and M. Olzmann, Phys. Chem. Chem. Phys., 2015, 17, 19862–19873.
50 L. I. Stiel and G. Thodos, AIChE J., 1964, 10, 266–269.
51 F. Temps and H. G. Wagner, Ber. Bunsenges. Phys. Chem., 1984, 88, 415–418.
52 G. Stark, P. L. Smith, J. Rufus, A. Thorne, J. Pickering and G. Cox, J. Geophys. Res., 1999, 104, 16585–16590.
53 T. A. Stephenson and M. I. Lester, Int. Rev. Phys. Chem., 2020, 39, 1–33.