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Direct evidence for a substantive reaction between the Criegee intermediate, CH_2OO, and the water vapour dimer

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Abstract

The C1 Criegee intermediate, CH_2OO, reaction with water vapour has been studied. The removal rate constant shows a quadratic dependence on $[H_2O]$, implying reaction with the water dimer, $(H_2O)_2$. The rate constant, $k_{CH2OO+(H2O)2}$ = (4.0 ± 1.2) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, is such that this is the major atmospheric sink for CH_2OO.

The Criegee intermediate is the long postulated intermediate formed in the ozonolysis of alkenes.[1] Even though much effort had gone into its direct observation from ozonolysis reactions, it has only recently been directly observed at low pressures via production in the reaction:[2]

$$CH_2I + O_2 \rightarrow CH_2OO + I \qquad R1a$$

This reaction is only just exothermic and is the near exclusive channel at low pressure.[3] As the total pressure is increased the mechanism for this reaction switches to an association process:

$$CH_2I + O_2 (+M) \rightarrow CH_2IO_2 \qquad R1b$$

where at atmospheric pressure the CH_2OO yield is 0.18.[3] Therefore this reaction and analogues using larger organic di-iodides are convenient sources of Criegee intermediates over a wide range of pressures, and in the last few years there has been a plethora of studies [4-7] that have used this type of reaction to determine direct properties of the Criegee intermediate, including the C2 species CH_3CHOO.[8]

Many of these new direct kinetic measurements on Criegee intermediates have determined rate constants significantly higher than older, indirect studies and their importance in atmospheric chemistry has been re-evaluated, in particular its reaction with SO_2 in competition with unimolecular decomposition [9] and photolysis.[4,10] The importance of these latter processes remains uncertain. An intriguing result of this new work on the Criegee intermediate is its reaction with H_2O:

$$CH_2OO + H_2O \rightarrow \text{Products } (HO\text{-}CH_2OOH)\ ^{11} \qquad R2$$

Only upper limits have been placed on this reaction rate constant (cm^3 $molecule^{-1}$ s^{-1}): $k_2 < 4 \times 10^{-15}$ from Welz *et al.*[2] via direct detection; $< 9 \times 10^{-17}$ from Stone *et al.*[12] via direct detection of the CH_2O product, and $< 2 \times 10^{-17}$ from Ouyang *et al.*[13] via detection of NO_3. In contrast to these results, end product analysis studies of ethylene ozonolysis, which exclusively generates only the C1 Criegee intermediate, have observed reaction with added water, with implied rate constants of 9×10^{-15} from Suto *et al.* [14] and 3×10^{-14} cm^3 $molecule^{-1}$ s^{-1} from Becker *et al.*[15] Most recently Berndt *et al.* [16] used ethylene ozonolysis to show that CH_2OO removal has a quadratic dependence on water vapour, which implies that it is water dimer that is reacting. Ozonolysis generates the Criegee intermediate via a highly exothermic reaction while reaction R1 is only just exothermic, so there is the possibility that the lack of reactivity of CH_2OO with H_2O in direct time-resolved experiments might be a consequence of its method of preparation: "hot" CH_2OO from ozonolysis might intercept H_2O but via R1 H_2O only

encounters "cold" CH_2OO. This effect is known as non-thermal kinetics and it has recently been demonstrated for the reaction of between OH and C_2H_2 in the presence of O_2.[17]

In this communication we demonstrate that by generating the Criegee intermediate using reaction R1 and directly following it in time via UV/VIS spectroscopy, reaction is observed with H_2O vapour that is described by a quadratic dependence on $[H_2O]$. This observation confirms reaction of the Criegee intermediate with the water dimer and that there is no significant difference in Criegee intermediate chemistry whether the intermediate is generated via reaction R1 or by ozonolysis.

The experiments were carried out using our newly constructed multiplexing absorption kinetics spectrometer coupled to laser flash photolysis. Full details about the setup will be described in a forthcoming publication. The essential details are as follows: the output from a xenon lamp was multi-passed 14 times through the 1.5 metre reaction cell and configured such that this probe beam was overlapped for the majority of this distance with the 248 nm excimer laser that passed along the length of the reactor. This probe beam was then directed via a fibre optic into a spectrograph (Jobin Yvon CP140-103) where the wavelengths 250 – 850 nm were simultaneously measured using a CCD image sensor (Hamamatsu S7031, back-thinned FFT-CCD). All the wavelengths were recorded for 1 millisecond intervals for a total of 200 milliseconds and transferred to a PC via a PCI interface board. All these data were processed by the PC using a custom built LabView program before the next photolysis laser pulse; the excimer laser was fired between 1 – 0.2 Hz. At each wavelength(λ), the 50 points before the excimer laser pulse were averaged and assigned to $I_0(\lambda)$ (intensity of the probe light), and all these $I_0(\lambda)$ were compared to all the wavelength time points after the excimer laser fired, $I(\lambda)$. The program calculated $\Delta I/I_0$ for each wavelength versus time, the time-resolved differential absorption signal for each wavelength.

An example of a spectrum at early time after photolysis is shown in Figure 1, where it can be seen that the spectrum between 300 – 400 nm is dominated by the C1 Criegee intermediate. At longer wavelengths absorption by the IO radical is also observable (CH_2I_2 photolysis produces a small amount of CH_2, which reacts with O_2 to produce $O(^3P)$[18] which in turn reacts with the precursor to produce IO[19]). The IO is removed from the system much more slowly than CH_2OO. H_2O vapour was added to the system by passing the main gas, N_2 (BOC, OFN), through a bubbler filled with deionized water, where the pressure in the bubbler was measured and could be varied over range 1000 – 2000 Torr. $[O_2]$ ($\sim 2 \times 10^{17}$ molecule cm^{-3}) was high enough to ensure R1 was rapid and the total pressure

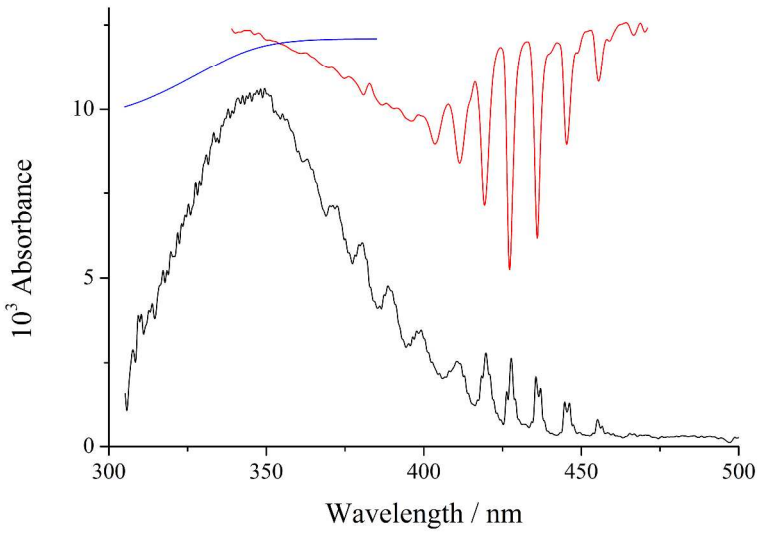

Figure 1. $\Delta I/I_0$ spectrum of the system at early-times over the wavelength range 300 – 500 nm. CH_2I_2 was photolysed at 248 nm (energy ~ 50 mJ/pulse/cm^2) in the presence of O_2: total pressure (N_2), O_2, CH_2I_2 and H_2O equal 1.52×10^{18}, 1.77×10^{17}, ~3 $\times10^{13}$ and 2.2×10^{16} molecule cm^{-3}, respectively. The spectrum was recorded 1 milli-second after the photolysis laser. The sharp peaks in the spectrum above 400 nm are due to IO, while the spectrum between 300 – 460 nm is the C_1 Criegee intermediate, CH_2OO. In red and blue the literature spectra of IO and CH_2I_2 (inverted to aid clarity) have been added to guide the eye.

was varied between 50 – 400 Torr, where N_2 was the main buffer gas. At each pressure the kinetics of the system were recorded without H_2O vapour and then the N_2 flow was switched to the H_2O bubbler, where the pressure can be adjusted. These experiments were carried out at 294 K.

The features of the spectrum in Figure 1, especially between 350 – 420 nm, are consistent with the absorption literature spectrum of CH_2OO.[20, 21] However, the present experiment records the differential absorption spectrum, $\Delta I/I_0$, and it needs to be corrected for CH_2I_2 photolysis and IO before it can quantitatively be used to compare to the literature. Also, the spectrum is Figure 1 has been corrected for scattered photons (>850 nm) hitting the CCD camera, see SI for further details. Hence this work cannot be compared with absolute cross-sections from any previous study at present. It is at 350 nm where the cross-section value reported by Ting *et al.*[22] is ca. a factor of three times lower than the values reported by Beames *et al.*[4] and Sheps.[21] In our previous study using a completely different absorption setup on CH_2I_2 photolysis in the presence of O_2 at atmospheric pressure we mis-assigned the Criegee intermediate spectrum as the CH_2IOO from reaction R1b.[23] If we now re-assign this spectrum as CH_2OO and divide the cross-sections by 0.18, which our recent measurements have determined as the yield of Criegee intermediate

at atmospheric pressure,[3] the spectrum is 40% lower at 350 nm than the cross-section value of Ting *et al.*[22]

If the reaction of CH_2OO with water is slow, then self-reaction [6] should dominate CH_2OO decay. The CH_2OO kinetic traces were analysed using an expression for second-order loss and it was observed that they were always better described by first-order kinetics, even for the traces at the lowest total pressure, see Figure 2 for example. At this stage it is not clear what is causing the unexpected first order kinetics; a possible explanation is unimolecular decay:[7,9]

$$CH_2OO \rightarrow \text{products} \qquad \text{R3}$$

It should be emphasised that experiments were always carried out in the absence of water vapour and then in the presence of water vapour, and therefore the difference between the pseudo-first-order decays can be attributed to the presence of water. The reaction with H_2O vapour is slow but it will be pseudo-first-order, and reaction of the Criegee intermediate with water vapour is only significant at the higher total pressures, where more water vapour can be added. Therefore it is reasonable to describe the Criegee intermediate loss as a first-order process:

$$[CH_2OO] = [CH_2OO]_0 \exp(-k_{obs}t) \qquad \text{E1}$$

where $k_{obs} = k_2' + k_3$, where $k_2' = k_2[H_2O]$ and k_3 is the first-order rate constant for CH_2OO removal other than H_2O and was typically ~ 200 s^{-1}. It is noted that in the study by Sheps [21] using similar concentrations (~ 5 $\times 10^{11}$ molecule cm^{-3}) the loss of CH_2OO was also observed to be reasonably described by single exponential behaviour and k_{obs} was comparable (180 s^{-1}) to this study. Second-order CH_2OO loss rate constants have been measured in studies [20, 24] that have used much higher concentrations than used in the present study.

The early-time spectrum in Figure 1 shows that both CH_2OO and IO are present and from Figure 2 it can be seen that the CH_2OO is removed much faster than IO under all conditions, especially at high water vapour concentrations. The data were analysed at five different wavelengths, 353, 350, 346, 344 and 341 nm, using the equation:

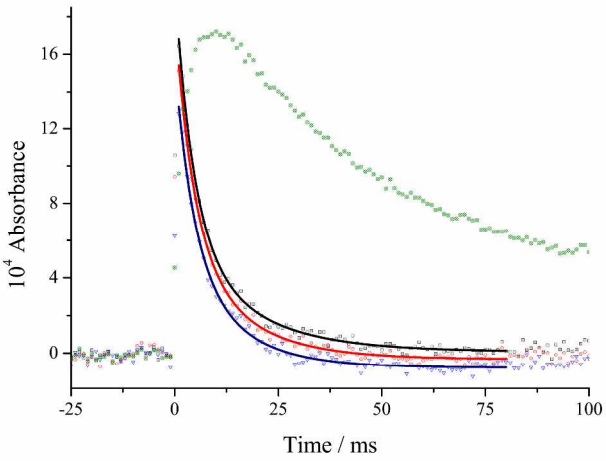

Figure 2. $\Delta I/I_0$ versus time traces for wavelengths that correspond predominantly to the Criegee intermediate (black- 353 nm, red – 350 nm and blue – 344 nm) and IO (green 436 nm). Traces at 341 and 346 nm have been omitted for clarity. CH_2I_2 was photolysed at 248 nm (energy ~ 50 mJ/pulse/cm^2) in the presence of O_2: total pressure (N_2), O_2, CH_2I_2 and H_2O equal 1.52×10^{18}, 1.77×10^{17}, $\sim3\times10^{13}$ and 2.2×10^{16} molecule cm^{-3}, respectively. The Criegee intermediate removal under all conditions is much faster than IO removal. The above data returns $k_{obs} = 221 \pm 17$ s^{-1}.

$$[CH_2OO] = [CH_2OO]_0 \exp(-k_{obs}t) + [B]_0 \exp(-k_b t) + C \qquad \text{E2}$$

where $[B]_0\exp(-k_bt)$ takes into account the small but significant contribution to the absorption from IO, k_b is the rate constant for IO loss, and C takes into account CH_2I_2 photolysis, which is significant up to 400 nm. In this analysis all the data at the five wavelengths were fitted simultaneously using equation E2, where k_{obs} was treated as a global parameter and all the other parameters were local. At each total pressure the k_{obs} was determined in the presence, $k_2' + k_3$, and absence of H_2O, k_3. Therefore subtracting k_{obs} with and without H_2O gives k_2'. As can be seen in Figure 2, the fits to the data were good and k_{obs} was defined with errors always less than 10 %. The validity of using equation E2 is that k_{obs} and not k_b is significantly changing as $[H_2O]$ is added to the system, and therefore k_{obs} vs $[H_2O]$ is a good measure of reaction R2.

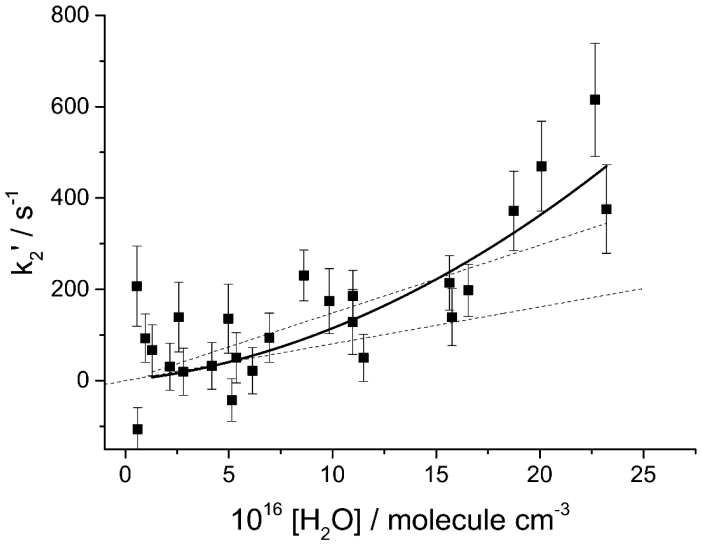

Figure 3. Bimolecular plot of the removal rate constant, k_2', in the presence of H_2O vapour, which exhibits distinct upward curvature. The solid line is the least squares fit of a quadratic function to the data, and yields a $\chi^2 = 37.5$. The dashed lines are linear least squares fits to the data over the full range and [H_2O] < 7.5×10^{-16} molecule cm^{-3}, 13 points. The slopes and χ^2 are 1.5 and 0.8×10^{-15} cm^{-3} $molecule^{-1}$ s^{-1} and $\chi^2 = 45.3$ and 9.2, respectively. The 20% improvement in the fit of the quadratic over the linear function, together with the increases in slope and χ^2 over the two H_2O ranges, highlights the curvature in the data. The [H_2O] was varied as the total pressure was varied between 50 – 400 Torr.

In Figure 3 k_2' is plotted versus the H_2O vapour concentration, and from this figure it is clear that at the highest concentrations the Criegee intermediate is reacting with water. However, closer inspection of this plot indicates that its dependence on H_2O concentration is better described by a quadratic rather than a linear dependence. The data are better described by a quadratic function based on the value of χ^2. Also shown in Figure 3 are linear least squares fits to the data over the full range and [H_2O] < 7.5×10^{-16} molecule cm^{-3}, 13 points, where it can be observed that there is a factor is two increase in the slope. These observations, together with visual inspection, highlight the curvature in the data. This observation is in agreement with the recent paper by Berndt *et al.* [16] where, from ozonolysis of ethylene, the removal of the Criegee intermediate (versus reaction with SO_2) was shown to have a quadratic dependence on [H_2O]. In Figure 4, k_2' is plotted versus [$(H_2O)_2$] [25] and it can be seen that the data are now better described by a linear relationship; good evidence that the Criegee intermediate is reacting predominantly with the dimer. The [$(H_2O)_2$] was calculated using the parameterisation of Scribano *et al.*,[25] which is the same calculation as used by Berndt *et al.*[16] Therefore the results from

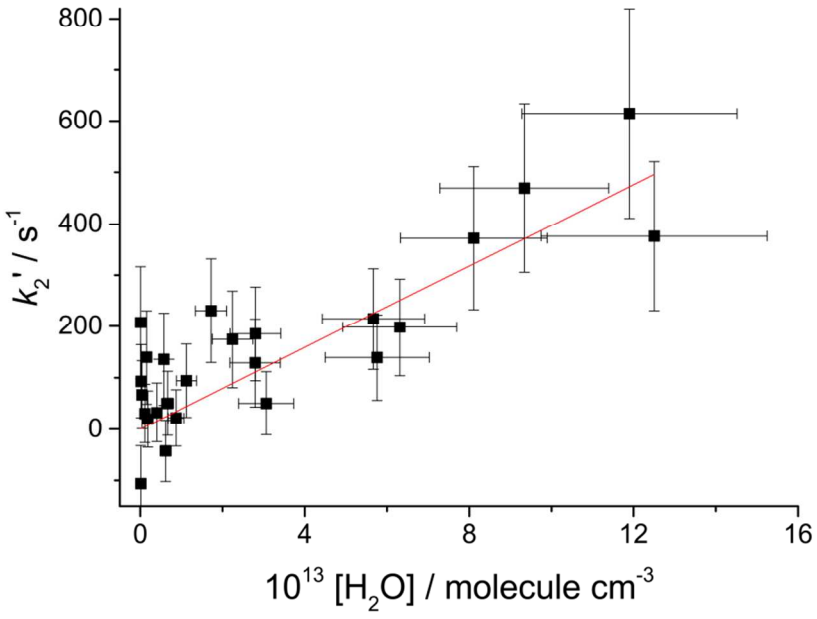

Figure 4. Plot of the removal rate constant, k_2', in the presence of $(H_2O)_2$. The plot is reasonably linear and yields a bimolecular rate constant, $k_4 = (4.0 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, 2σ error. X-errors are estimated to be 22% and are propagated into the k_4 determination.

this study can be directly compared to Berndt *et al*. even though there is an estimated 20% error in the water dimer concentration.

The slope of Fig 4 is equal to the rate constant for the bimolecular reaction:

$$CH_2OO + (H_2O)_2 \rightarrow HO\text{-}CH_2OOH + H_2O \quad [26] \qquad \text{R4}$$

The rate constant for reaction k_4 is equal to $(4.0 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and includes uncertainty due to [H_2O](10%) and [H_2O]$_2$ (20%). In the *ab initio* calculations by Ryzhkov *et al.*[26] the channel to HO-CH_2OOH (HMHP) was observed to be the lowest energy for both H_2O (R2) and $(H_2O)_2$ (R4), with the dimer reacting to a greater extent under atmospheric conditions. It is noted that the present data could have a contribution from reaction R2, and therefore k_4 should be regarded as an upper limit. However, in the *ab initio* study by Ryzhkov *et al.* [26] the calculated ratio of rate constants (k_2/k_4) is 3×10^{-5}. At [H_2O] = 2×10^{17} molecule cm^{-3} the concentration of [H_2O]$_2$ is 9×10^{13} molecule cm^{-3}, therefore the contribution from R2 is 0.07, and is only has a minor contribution in the present measurements. In the SI we report analysis of the data where both k_2 and k_4 are considered, and it is concluded that k_4 is overestimated by no more than 20%.

The value reported by Berndt *et al*. was $k_4 = 1.01 \pm 0.03 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is about a factor of two larger than our present value. So while both studies are in broad agreement in that reaction R4 is operating, there is a significant discrepancy in the magnitude of the rate constant. In the present work, the rate constant k_4 is extracted from the change in k_{obs} on addition of water vapour, where $k_2' / k_3 < 10$ and hence leads to larger than usual error in the bimolecular rate constant, see Figure 4, but not as high as a factor of two. [H_2O] was determined from measuring the temperature and pressure of the bubbler and it was assumed that the entire H_2O equilibrium vapour pressure was delivered to the reactor. This is normally a reliable method to estimate the concentration of species introduced via a bubbler; previous work using a bubbler to deliver amines to a kinetic experiment has shown good agreement between calculated concentrations and values measured directly in the cell via UV absorption.[27] However, it is acknowledged that there is a potential to overestimate the water vapour concentration. Alternatively, there may be another reason for this discrepancy. The experiments from Berndt *et al.*[16] used an atmospheric pressure time-of-flight mass spectrometer, where gas was sampled via a small aperture into the low pressure environment of the mass spectrometer. This gas expansion promotes cooling, which promotes dimer formation, and if dimer formation is promoted more rapidly than the reduction in pressure then Criegee intermediate loss inside the mass spectrometer increases. While this is speculative there are examples of promoted chemistry inside this type of mass spectrometer.[28] At the moment the source of this difference in the rate constant is unclear but it is clear that the Criegee intermediate generated via reaction R1 or via ozonolysis produces essentially the same chemistry, i.e. there is no non-thermal kinetics.

This brings into question the failure of previous studies to observe any reaction of CH_2OO with H_2O vapour. In the experiments by Welz *et al.*[2] the Criegee intermediate was directly monitored and the highest amount of [H_2O] added was 3×10^{16} molecule cm^{-3} (corresponding to 2×10^{12} molecule cm^{-3} dimer). This amount of [H_2O] increases the rate constant by no more than 20 s^{-1}, which in the experiments of Welz *et al.* is too small to observe. In the experiments by Stone *et al.*[12] CH_2O was used to follow the Criegee kinetics in time and up to [H_2O] = 1.7×10^{17} molecule cm^{-3} (corresponding to 6×10^{13} molecule cm^{-3} dimer) was added to the system. The calculated increase in the Criegee intermediate removal rate constant is between 250 – 600 s^{-1} and should be measurable. However, this method relies on CH_2O only coming from characterised CH_2OO and CH_2IO_2 chemistry. If the products of reaction R4 bring about new chemistry that forms CH_2O then it could mask any reaction with H_2O vapour. This new chemistry would be from radical-radical reactions. Therefore in the experiments of Stone *et al.* [12] where the radical densities are a few 10^{12} molecule cm^{-3} CH_2O could be

formed on a timescale not incompatible with this possible explanation. In the experiments of Ouyang *et al*.[13] Criegee intermediate kinetics with H_2O were determined in competition with NO_2 by following the NO_3 formed from $CH_2OO + NO_2$. In these experiments up to 6×10^{17} molecule cm^{-3} of H_2O (corresponding to 8×10^{14} molecule cm^{-3} dimer) was added to the system, therefore the Criegee intermediate removal rate constant should have been > 3000 s^{-1}, but no removal was observed. However, this method is dependent on Criegee intermediate + NO_2 reacting to make NO_3. The experiments by Ouyang *et al*.[13] were not time-resolved; the contents of the reactor flowed into a cavity spectrometer and therefore it is possible that other secondary chemistry was responsible for NO_3 production. In a forthcoming paper it will be demonstrated using the current flash photolysis / UV/VIS absorption setup that NO_3 is not significantly made by reaction of Criegee with NO_2, and the small amount of observed NO_3 is consistent with the iodine chemistry, $INO_2 + IONO_2 \rightarrow NO_3 + NO_2 + I_2$. Therefore the lack of change in the NO_3 signal versus added H_2O indicates a lack of reactivity in iodine chemistry and not Criegee intermediate chemistry.

Conclusions

The Criegee intermediate, CH_2OO, has been observed to react in the presence of water vapour. This is the first direct measurement to show that this reaction is occurring and its kinetics implies that the reaction is predominantly with the water dimer, $(H_2O)_2$, where $k_4 = (4.2 \pm 1.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. This result is in support of the recent indirect measurements by Berndt *et al*.[16] and indicates that Criegee intermediate chemistry is essentially independent of the method of generation via either ozonolysis or iodo-alkyl radical + O_2. The observed loss contrasts with other previous studies, but we believe the discrepancies can be explained by either the use of relatively low concentrations of water (limiting dimer formation) or via secondary chemistry in more indirect studies monitoring products. The direct observation of Criegee intermediates as used in this study will be less susceptible to such systematic errors.

Using the representative range in $(H_2O)_2$ concentrations (molecule cm^{-3}) reported by Vereecken *et al*.,[29] 8.5×10^{13} (mega city) to 5.5×10^{14} (tropical forest), results in first-order loss rate for C1 Criegee intermediate ranging from 357 - 2310 s^{-1}. This is significantly greater than first order loss rates with other trace gases. In the atmospheric implications from Vereecken *et al*. [29] reaction R4 was included, using a theoretical estimate of the rate constant, and it was concluded that water vapour was the dominant removal process. This assessment provides a better representation of Criegee chemistry

compared to modelling studies that have not included reaction R4.[30] Given the importance of Criegee intermediates, further studies of the reaction with water dimer are required to confirm the fast kinetics reported in this work and to identify the products of the reaction.

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