

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

Supporting Information

Problems with the current absorption spectrometer

In the current newly constructed kinetics absorption spectrometer absolute cross-sections were not assigned to the C1 Criegee intermediate for a number of reasons. An interesting feature that is a little surprising with the current apparatus is false photons hitting the CCD camera below 400 nm, but is very significant below 320 nm; the corresponding 250 nm pixel was saturated because of this problem. Tests by the manufacturer (Entwicklungsbuero Stresing, <http://www.stresing.de/>) showed that NIR light from the Xe arc lamp exits the spectrograph and hits the connecting ring between the spectrograph and the CCD. This NIR light was scattered onto the UV end of the CCD camera. To correct for this effect spectra were recorded for O_3 and NO_2 and were compared to the literature. The correction factor is equal to the ratio of the recorded spectrum to the literature. Figure S1 shows this effect by comparing spectra with and without the correction factor. This problem can be fixed to some extent by blacking the connecting ring, but tests still reveal that there still needs to be a correction made below 300 nm.

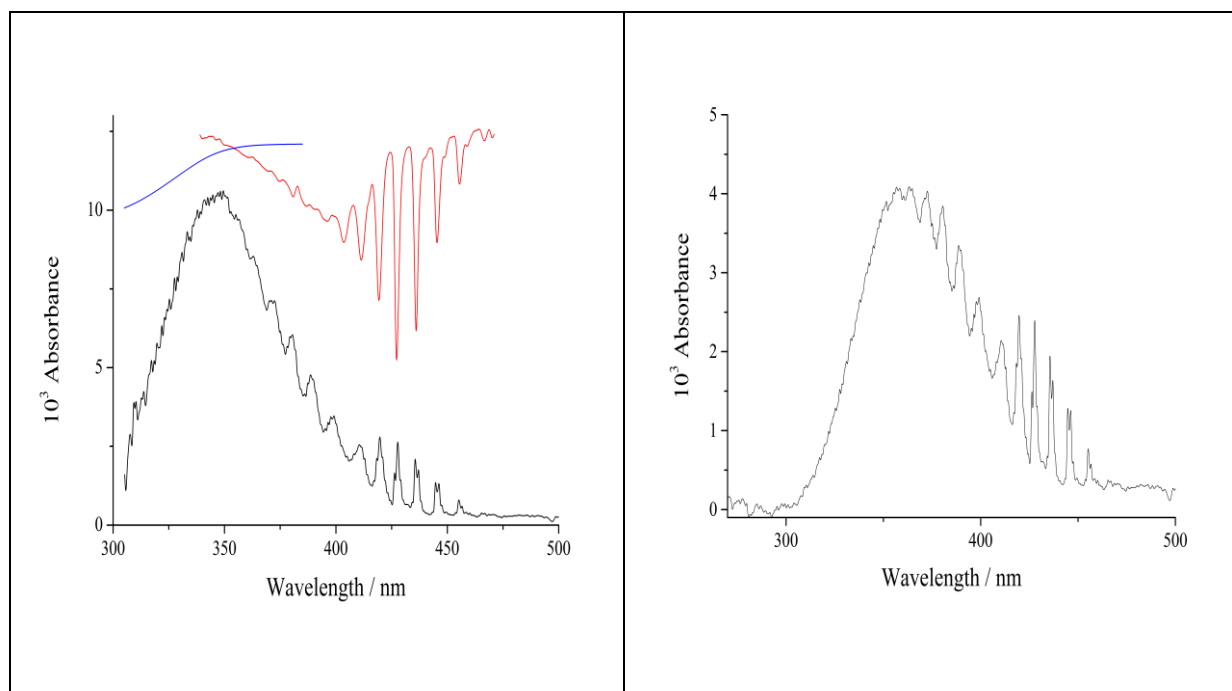


Figure S1. The above figures demonstrate our NIR scattering problem, where the NIR (>850 nm) scatters off the connecting ring between the spectrograph and the CCD camera. The spectrum on the right is the uncorrected data and the one on the left is the corrected data. There is no correction to the spectrum at $\lambda > 400$ nm, but it is evident below. The correction factor $\lambda < 310$ nm is greater than a factor of 10.

Regarding the reliability of the [H₂O] and [H₂O]₂

H₂O vapour is a notoriously sticky molecule to flow through the system. The most reliable way to put a known amount through a system is via a bubbler at a stable temperature, as we have done here. So the water concentration – x-error – has a much larger error than the error returned from the data analysis for individual points. For this reason we propagated a 50 s⁻¹ error with all the returned errors in k_{obs} . The reason why the data are so scattered is largely due to difficulty in handling such a sticky molecule.

Regarding the water dimer concentration, the main text states that we are using the water equilibrium dimer parameterisation by Scribano et al.²⁵ in order to calculate the water dimer concentration and assign the CH₂OO + (H₂O)₂ rate constant. This is the same calculation as Berndt et al.¹⁶ so we can directly compare our data. From Scribano et al.²⁵ it is recognised that the equilibrium constant for (H₂O)₂ formation has significant uncertainty. From the paper Scribano it is estimated that the uncertainty in the equilibrium constant close to room temperature is no more than 20%.

Overall we estimate there is a 10% error in the [H₂O] and 20% in the [H₂O]₂. In Figure 4 we propagate this x-error, 22%, into the y error in order to obtain a better estimate of the error in k_4 .

Including both k_2 and k_4 in the analysis

If the CH₂OO reaction is only occurring via R4 then the dependence on [H₂O] is equal to

$$k_2' = C1 \times [\text{H}_2\text{O}]^2 \quad \text{E1}$$

where C1 is the constant related to the H₂O to H₂O₂ equilibrium constant¹ and k_4 . If both reaction R2 and R4 are occurring then

$$k_2' = k_2[\text{H}_2\text{O}] + C1 \times [\text{H}_2\text{O}]^2 \quad \text{E2}$$

Analysing the data using E2 returns a value for $k_2 = (4.9 \pm 5.1) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is consistent with the upper limit of $< 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Welz *et al.*², but inconsistent with the limits reported by Ouyang *et al.*³ ($< 2 \times 10^{-17}$) and Stone *et al.*⁴ (9×10^{-17}). In the studies of Stone et al. and Ouyang *et al.*³ the products (CH₂O and NO₃) of the Criegee reaction were monitored and assumed to be from the Criegee reaction. This present study indicates that these monitored products are not uniquely from Criegee

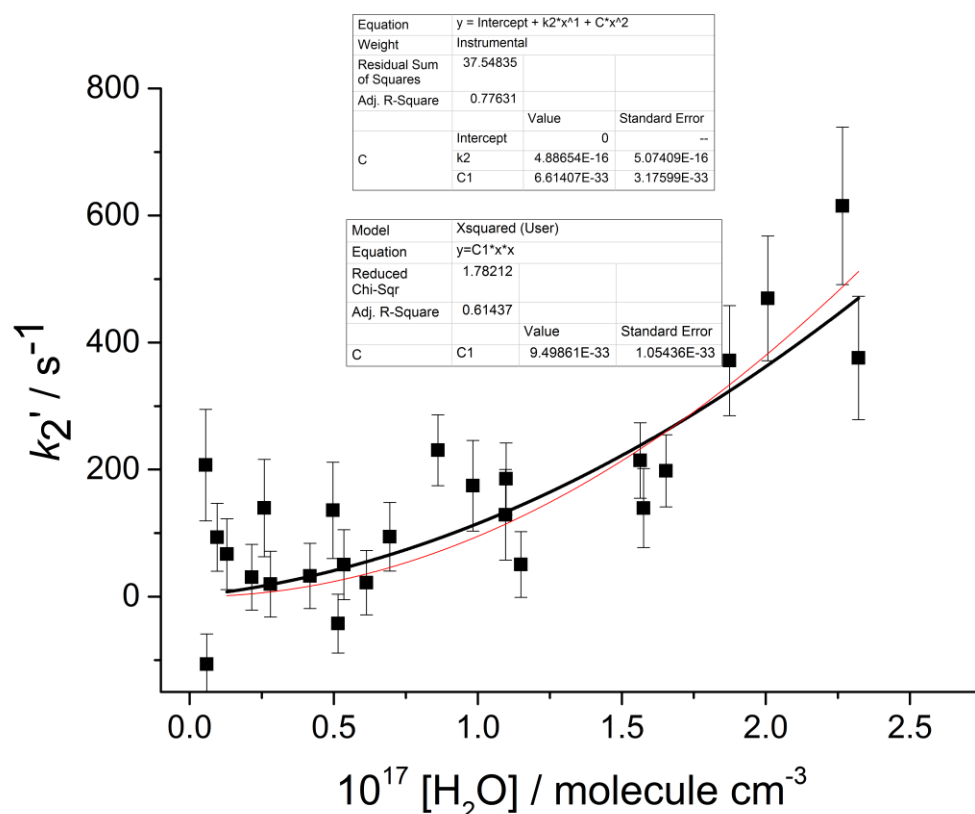


Figure S2. Fits to the removal rate constant, k_2' , in the presence of $(\text{H}_2\text{O})_2$: the black is the fit using equation E1 and the red is the fit using equation E2.

reaction. Hence the assigned reaction rate constant between CH_2OO and water vapour by Ouyang *et al.* and Stone *et al.* is most likely incorrect.

Fitting the data to equation E1 yields an essentially equal fit compared to E2, see Figure S2. As k_4 is proportional to the square root of $C1$, $\sqrt{C1}$, therefore comparing $\sqrt{C1}$ returned from the fits using E1 and E2 indicates that by not including reaction R2 in the analysis will overestimate k_4 by no more than 20%. In the main text R2 is not included in the analysis.

References

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