

# On the Impact of HO<sub>2</sub>-H<sub>2</sub>O Complexes in the Marine Boundary Layer: A Possible Sink for HO<sub>2</sub>

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## ABSTRACT

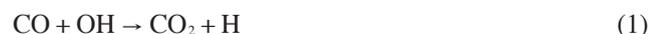
The impact of the formation of HO<sub>2</sub>-H<sub>2</sub>O adducts following reaction between H<sub>2</sub>O and HO<sub>2</sub> and subsequent reaction of this adduct on HO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> as a function of relative humidity in the marine boundary layer has been investigated using a zero-dimensional box model. The results of simulations with different product yields for the reaction of HO<sub>2</sub>-H<sub>2</sub>O with HO<sub>2</sub> were compared with base case data derived from current recommendations for tropospheric modelling. It is suggested that inclusion of reactions of the HO<sub>2</sub>-H<sub>2</sub>O adduct may provide a significant sink for HO<sub>2</sub> which has so far not been considered in models of tropospheric chemistry and depending on reaction products may have a significant impact on H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>.

Key words: HO<sub>2</sub>-H<sub>2</sub>O complexes, Master chemical mechanism, CRI mechanism, Marine boundary layer, Criegee biradicals

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## 1. INTRODUCTION

The hydroperoxy radical (HO<sub>2</sub>) is the first in the series of radical intermediates that are known as peroxy radicals. Peroxy radicals (RO<sub>2</sub> where R can be an alkyl, aryl or allyl group) are ubiquitous in the troposphere. The major background source of HO<sub>2</sub> is through the oxidation of CO:



HO<sub>2</sub> is the dominant member of the HO<sub>x</sub> family (HO<sub>x</sub> = HO + HO<sub>2</sub>) in terms of concentration, though not in terms of reactivity. Under very low NO<sub>x</sub> conditions the reaction of HO<sub>2</sub> with O<sub>3</sub> is a non-negligible source of the hydroxyl radical (OH), itself the primary oxidant in the troposphere. Partitioning of HO<sub>x</sub> into OH and HO<sub>2</sub> is dependant in part on reaction (3):



Of particular importance then to the HO<sub>x</sub> cycle is the recombination reaction (4) for HO<sub>2</sub> as this directly affects the HO<sub>x</sub> balance as the product H<sub>2</sub>O<sub>2</sub> is highly soluble and is readily washed out of the atmosphere through precipitation.



As a result of the importance on the HO<sub>x</sub> budget the recombination reaction has been the subject of many investigations in the gas phase (Stone and Rowley 2005 and references therein). It is known to show some interesting behaviour, exhibiting both bimolecular and termolecular components and with each showing a negative temperature dependence and most significantly displaying a rate enhancement in the presence of H-bonding partners. The most atmospherically important component of these observations is the enhancement of the reaction in the presence of H<sub>2</sub>O. The first study to investigate this facet of the reaction was performed by Hamilton (1975). Since then it has been widely observed

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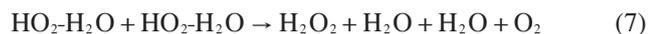
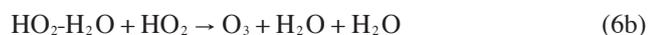
that the rate of the reaction shows a linear dependence on the partial pressure of H<sub>2</sub>O employed in the study.

The current understanding for the water enhancement on the rate observed in laboratory studies is attributed to the formation of an HO<sub>2</sub>-H<sub>2</sub>O adduct. The existence of an HO<sub>2</sub>-H<sub>2</sub>O adduct has received a modest amount of interest, both experimental (Aloisio and Francisco 1998; Aloisio et al. 2000; Kanno et al. 2005, 2006; Suma et al. 2006) and theoretical (Zhu and Lin 2002, 2003; Alongi et al. 2006) studies have recently been performed to understand its formation and subsequent reactivity. Kanno et al. (2005) studied the kinetics of the HO<sub>2</sub>-H<sub>2</sub>O adduct and concluded that at 297 K and 50% relative humidity (RH) [HO<sub>2</sub>-H<sub>2</sub>O]/[HO<sub>2</sub>] = (0.19 ± 0.11). This was further confirmed in the study by Alongi et al. (2006) who concluded that with HO<sub>2</sub> concentrations on the order of 10<sup>8</sup> molecules cm<sup>-3</sup> the HO<sub>2</sub>-H<sub>2</sub>O concentration at 50% RH would be on the order of 10<sup>7</sup> molecules cm<sup>-3</sup>.

In our study we have looked at the impact of the formation of a HO<sub>2</sub>-H<sub>2</sub>O adduct on the products of the recombination reaction. The HO<sub>2</sub>-H<sub>2</sub>O adduct is formed from an equilibrium described by reactions (5) and (-5).



The HO<sub>2</sub>-H<sub>2</sub>O adduct can then go on to react with HO<sub>2</sub> through reactions (6a) and (6b) or it can react with another HO<sub>2</sub>-H<sub>2</sub>O adduct (7).



The products of reaction (6b) have previously been believed to be associated with only a very small proportion of the reaction, less than 0.1% (Niki et al. 1980). However, ab initio calculations performed at the G2M(CC5) level of theory (Zhu and Lin 2003) have shown that the presence of the water adduct can greatly reduce the barrier to this reaction, which may make reaction (6b) competitive with reaction (6a).

In this study we have aimed to assess the impacts of including reactions of the HO<sub>2</sub>-H<sub>2</sub>O adduct on the HO<sub>2</sub> recombination reaction by studying the reactions at different RH using a numerical box model.

## 2. MODELLING

A simple numerical box model, BAMBO (Archibald et

al. 2009), was used in this investigation. The model simulates clean atmospheric conditions considering the marine boundary layer (MBL) as a representative environment. The model receives input of chemical species through emissions from the surface and mixing in from the free troposphere. Free tropospheric emissions are provided for relatively long lived species such as O<sub>3</sub>, CO, CH<sub>3</sub>OOH, PAN and some NMHCs (C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>) whilst surface emissions are provided for isoprene, ethene, propene, propane and dimethyl sulfide (DMS) (average mixing ratios and atmospheric parameters can be found in Table 1). A comprehensive chemical mechanism is employed based on the MCMv3.1 (Saunders et al. 2003) which details near explicitly the gas phase degradation of methane; ethane; ethene; propane; propene; n-butane; isoprene and DMS. Halogen chemistry has been added to the mechanism based on the work of Toyota et al. (2004), McFiggans et al. (2000) and recent IUPAC and JPL recommendations (Sander et al. 2003; Atkinson et al. 2006). However, for the model runs discussed in this article we have not considered the influence of halogen chemistry so have used a zero flux of halogenated species. Dry deposition is considered for selected species with the corresponding deposition rates ( $v_d$ ) for O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, being 0.05, 1.00, 1.00, and 0.70 cm s<sup>-1</sup> respectively.

Photolysis coefficients ( $j_i$ ) are calculated using the MCM protocol of relating  $j_i$  to the secant of the solar zenith angle,  $x$  described by Jenkin et al. (1997):

$$j_i = L \cos x^M \exp(-N \sec x) \quad (I)$$

where the coefficients  $L$ ,  $M$  and  $N$  are derived from a fitting procedure using the two stream radiative transfer model of

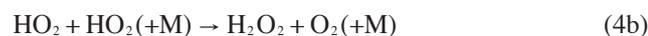
Table 1. Model parameters used in all runs.

Parameter	Value *
Temperature	288 K
Pressure	760 mb
Boundary layer height	700 m
RH	Variable, see text
CH <sub>4</sub>	1.76 pptv
CH <sub>3</sub> SCH <sub>3</sub>	190 pptv
C <sub>3</sub> H <sub>8</sub>	12.8 pptv
C <sub>2</sub> H <sub>4</sub>	58.7 pptv
C <sub>3</sub> H <sub>6</sub>	22.8 pptv
NO <sub>x</sub>	19.5 pptv

\* Average values at 80% RH.

Hough (1988). Integration of the chemical reactions is done using the FACSIMILE integrator (2007) which uses a Gears type predictor-corrector technique.

Four different sets of kinetic and product data were evaluated in the model runs, an overview of which can be found in Table 2. Run A was a base case run where the kinetic and product data for the HO<sub>2</sub> recombination reaction was taken from the most recent IUPAC recommendations:



For reactions (4a) and (4b) in the presence of water the current recommendation is to use the following expressions for the rate:

$$k_{4a} = 2.2 \times 10^{-13} \exp(600/T) \{1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)\} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k_{4b} = 1.9 \times 10^{-33} [M] \exp(980/T) \{1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)\} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

where M refers to the number density in molecules cm<sup>-3</sup>.

In runs B, C and D we have used the following expression for the bimolecular channel (4a) (Kanno et al. 2006):

$$k_{4a} = 1.9 \times 10^{-13} \exp(670/T) + 4.4 \times 10^{-14} \exp(980/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

and for the formation and decomposition of the HO<sub>2</sub>-H<sub>2</sub>O adduct (5) and (-5):

$$k_5 = 1.0 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k_{-5} = \frac{1.52 \times 10^{13}}{T \exp(3700/T)} \text{s}^{-1}$$

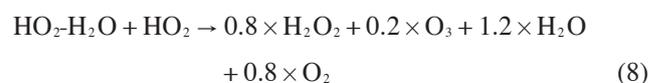
For run B the products of the subsequent reactions of the HO<sub>2</sub>-H<sub>2</sub>O adduct with HO<sub>2</sub> and with another HO<sub>2</sub>-H<sub>2</sub>O

adduct were described by reactions (6) and (7) with the rates being given by:

$$k_6 = 5.4 \times 10^{-11} \exp(-410/T) + 1.3 \times 10^{-11} \exp(-100/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

$$k_7 = 1.0 \times 10^{-15} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

The kinetic parameters for reactions (4) - (7) were kept the same for runs C and D but for run C the product yields of reaction (6) were 100% via channel (6b) and in run D the product yields of reaction (6) were changed to reaction (8):



Each model scenario was run at a variety of RH ranging from 5% to 100%. The corresponding diurnally averaged H<sub>2</sub>O mixing ratio at a specific RH is shown in Table 3 but it can be noted that by increasing the RH in the model run the H<sub>2</sub>O mixing ratio in the model increases.

### 3. RESULTS

The level of H<sub>2</sub>O<sub>2</sub> in the troposphere is highly variable (e.g., Olson et al. 1997; Morgan and Jackson 2002; Arakaki et al. 2005; Walker et al. 2006). However, inspection of measurement data for the marine boundary layer in summer would suggest that levels between 750 - 1500 pptv are reasonable. Therefore the base case simulation of around 1200 pptv at high humidity is well within the range of observed measurements. Results from the model runs are shown in Figs. 1 - 4. The results show data obtained from the tenth model day (when the model has settled into a repeating diurnal cycle) and show the average values obtained over that day. Figure 1 shows a plot of the average ratio of [HO<sub>2</sub>-H<sub>2</sub>O] to [HO<sub>2</sub>]. Using our box model we predict that at RH of 50% approx. 16% of HO<sub>2</sub> will be found as HO<sub>2</sub>-H<sub>2</sub>O. This is in good agreement with the previous estimates by Kanno et al. (2005) who suggested that at a RH of 50% up to (19 ± 11)% of HO<sub>2</sub> can be predicted to be found as HO<sub>2</sub>-H<sub>2</sub>O and

Table 2. Product information relating to the different model runs (see text for full description).

Run	Details of Run
A	BAMBO base case run using IUPAC recommendations for HO <sub>2</sub> + HO <sub>2</sub>
B	Products of HO <sub>2</sub> -H <sub>2</sub> O + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> + H <sub>2</sub> O
C	Products of HO <sub>2</sub> -H <sub>2</sub> O + HO <sub>2</sub> → O <sub>3</sub> + H <sub>2</sub> O + H <sub>2</sub> O
D	Products of HO <sub>2</sub> -H <sub>2</sub> O + HO <sub>2</sub> → 0.8 × H <sub>2</sub> O <sub>2</sub> + 0.2 × O <sub>3</sub> + 1.2 × H <sub>2</sub> O + 0.8 × O <sub>2</sub>

Table 3. Comparison of RH used in the model runs to average H<sub>2</sub>O concentration and H<sub>2</sub>O mixing ratio.

Relative Humidity	Average H <sub>2</sub> O concentration *	H <sub>2</sub> O atmospheric mixing ratio (%)
5.0	$2.07 \times 10^{16}$	0.08
10.0	$4.14 \times 10^{16}$	0.16
15.0	$6.21 \times 10^{16}$	0.24
20.0	$8.28 \times 10^{16}$	0.32
40.0	$1.66 \times 10^{17}$	0.65
60.0	$2.48 \times 10^{17}$	0.97
80.0	$3.31 \times 10^{17}$	1.30
100.0	$4.14 \times 10^{17}$	1.62

\* in units of molecules cm<sup>-3</sup>.

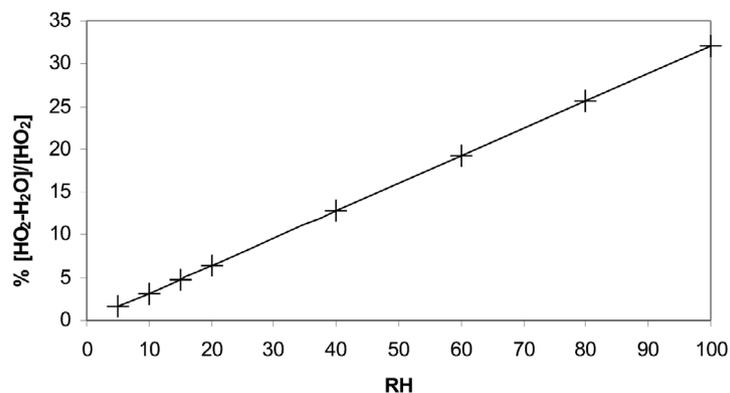


Fig. 1. Ratio of HO<sub>2</sub>-H<sub>2</sub>O to HO<sub>2</sub> versus relative humidity obtained from run B. In this plot we present the data for the average ratio of the mixing ratio of the HO<sub>2</sub>-H<sub>2</sub>O adduct to HO<sub>2</sub> over the model run against the relative humidity. It can be seen from this plot that as the RH increase so does the ratio of water adduct to HO<sub>2</sub> due to the increase in water vapour at higher RH.

Alongi et al. (2006) who estimate 10%. As we increased RH to 100% our model predicts that up to 30% of HO<sub>2</sub> could be found as HO<sub>2</sub>-H<sub>2</sub>O, in agreement with the original work of Aloisio and Francisco (1998). From Fig. 1 it is also possible to calculate the predicted atmospheric mixing ratios of the HO<sub>2</sub>-H<sub>2</sub>O adduct which our model estimates to be up to 1.8 parts per trillion by volume (pptv) at RH greater than 80%. There have yet to be any observations of this adduct in the field but there have been observations in laboratory studies (Aloisio et al. 2000; Suma et al. 2006). Based on the model predictions we would expect that under conditions of high RH with HO<sub>2</sub>-H<sub>2</sub>O in the atmospheric mixing ratio range of 1 - 3 pptv it may be possible for detection in the field.

The atmospheric implications of the presence and subsequent reaction of the HO<sub>2</sub>-H<sub>2</sub>O adduct can be seen from the plots of selected trace gases shown in Figs. 2 - 4. In Fig. 2 we present the average H<sub>2</sub>O<sub>2</sub> mixing ratio in pptv over the tenth model day at the different RH investigated for runs A - D. In all runs but C it can be observed that the H<sub>2</sub>O<sub>2</sub> mixing ratio increases with an increase in RH. The results from run B show an increase in H<sub>2</sub>O<sub>2</sub> by approx. 10% at

RH greater than 80%. In run C, where the products of the recombination reaction were set to channel (6b) i.e., 100% O<sub>3</sub>, the H<sub>2</sub>O<sub>2</sub> mixing ratio reaches a maximum at around RH 50% and then begins to dip at higher RH. When compared with the base case, run A, the maximum H<sub>2</sub>O<sub>2</sub> mixing ratio predicted in run C is 35% lower than the base case maximum. The H<sub>2</sub>O<sub>2</sub> results from run D, where a mixture of products for the recombination reaction were used, agree remarkably well with the base case data. It is suggested that this observation may support the possibility for a small O<sub>3</sub> channel for the recombination in the presence of water.

In Fig. 3 the O<sub>3</sub> variation is plotted and is shown to decrease with increasing RH. The decrease in O<sub>3</sub> with increasing RH can be attributed to the enhanced removal of O(<sup>1</sup>D) by reaction with H<sub>2</sub>O, leading to an increase in OH production at higher RH:



The agreement between runs A and B is very good. In run D there is a slight increase in O<sub>3</sub> production, equivalent to an increase of approx. 120 pptv averaged over all RH. However, in run C there is a pronounced increase in O<sub>3</sub> production, leading to an increase of up to 8% at RH greater than 80%.

In all cases in Fig. 4, HO<sub>2</sub> exhibits a rapid increase in concentration at low RH (< 30%) after which concentrations increase slowly and plateau around values of 80% - 100% RH. This structure is probably due to the superposition of decreasing O<sub>3</sub> with RH and increasing OH with RH. Clearly there is a noticeable difference in HO<sub>2</sub> concentrations derived from run A compared with runs B, C and D where inclusion of the formation and reactions of the HO<sub>2</sub>-H<sub>2</sub>O adduct leads to a constant decrease in HO<sub>2</sub> concentrations dropping down by 12% at RH greater than 80%.

The effect on OH was also investigated and the modelling results obtained demonstrate the general trend of increasing OH at higher RH through reaction (10). The agreement between each of the different model runs was very good with only a slight increase in OH being predicted at high RH from run C. This small increase is most likely due to the increased flux of O<sub>3</sub> and the subsequent reaction of O<sub>3</sub> reactions (9) and (10), i.e., producing OH.

#### 4. DISCUSSION AND CONCLUSION

The formation of the HO<sub>2</sub>-H<sub>2</sub>O adduct and subsequent reactions have been modelled using a zero-dimensional box model and the results at different RH have been compared with results using a base case scheme. The base case scheme used was based on the recent recommendations of IUPAC

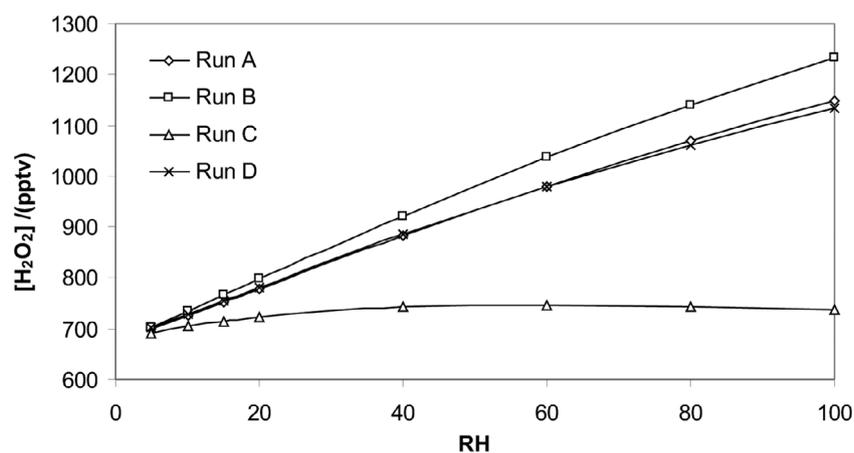


Fig. 2. H<sub>2</sub>O<sub>2</sub> variation with RH. The average H<sub>2</sub>O<sub>2</sub> mixing ratio is plotted against the RH used in the model run. A general trend in all but run C can be seen that increasing the RH will increase the H<sub>2</sub>O<sub>2</sub> concentration in the model. It can be seen that inclusion of the new data (open squares) results in a higher H<sub>2</sub>O<sub>2</sub> mixing ratio (approx. 100 pptv) than the base case (IUPAC recommendation) open diamonds.

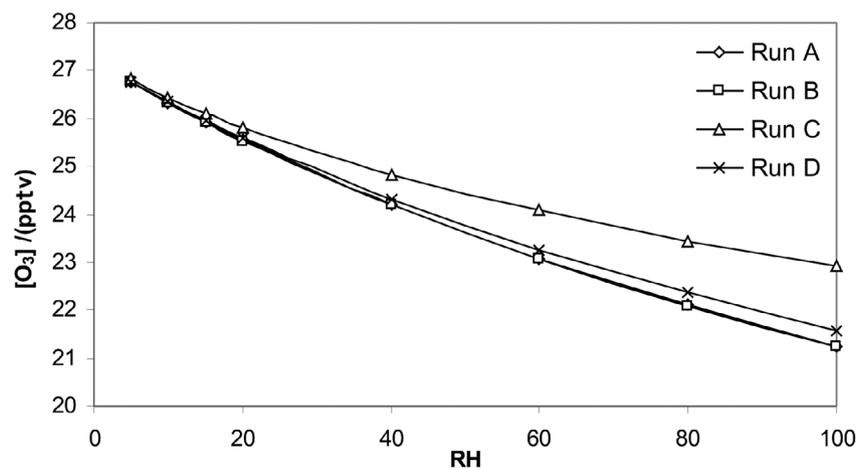


Fig. 3. O<sub>3</sub> variation with RH. The diel averaged O<sub>3</sub> from the tenth model day is plotted against the RH used in the model run. In all cases the average O<sub>3</sub> mixing ratio decreases with respect to increased RH. In runs C and D O<sub>3</sub> levels are shown to be approx. 2 and 0.3 pptv higher than the base case run respectively.

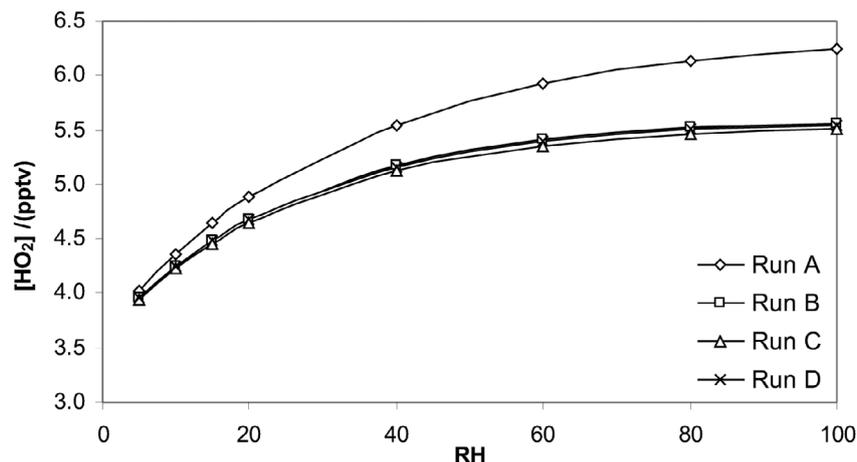


Fig. 4. Hydroperoxy radical variation with RH. Average HO<sub>2</sub> mixing ratios are plotted against RH and are shown to increase with RH most rapidly at lower RH. The inclusion of formation and reactions of the HO<sub>2</sub>-H<sub>2</sub>O adduct (runs B, C and D) is shown to produce a significant lowering in HO<sub>2</sub> (12%) compared with the base case.

(Atkinson et al. 2006) for the water enhancement of the HO<sub>2</sub> recombination reaction. The results of our study have shown that the model predicted concentrations of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> are dependent on the products of the reaction between the HO<sub>2</sub>-H<sub>2</sub>O adduct and HO<sub>2</sub>. Based on recent theoretical work (Zhu and Lin 2003) we have investigated the impact of O<sub>3</sub> as a product in the recombination reaction. Given that other studies such as that by Stone and Rowley (2005) have not observed any ozone formation following reaction (6) under elevated levels of H<sub>2</sub>O, it is suggested that the reaction is unlikely to proceed to give a unit yield of O<sub>3</sub> but it would be highly valuable to perform further experimental work to determine if there is a branching ratio to produce O<sub>3</sub> from this reaction. Given the flux of material through this reaction, even a small branching ratio to form ozone could be significant on a global scale.

It has been widely observed that when remote field measurements are compared with model results, modelled OH and HO<sub>2</sub> may be significantly higher than measurements (Kanaya et al. 2007 and references therein). Several possibilities for the high modelled HO<sub>2</sub> have been considered including, lack of heterogeneous loss, reactions with halogen oxides not being considered and poor representation of kinetics of RO<sub>2</sub> + HO<sub>2</sub> reactions. In this study we have focused on a relatively pristine environment and have neglected any interference by halogen chemistry or heterogeneous processes. However, by representing the HO<sub>2</sub> recombination using kinetic data from Kanno et al. (2006) we have found that a new loss process for HO<sub>2</sub> is through the formation of an HO<sub>2</sub>-H<sub>2</sub>O adduct. Of course, current models do take into consideration the pressure and water dependence of the self reaction of HO<sub>2</sub> radicals, but we show that there is a difference between using such a parameterisation and modelling the formation and loss of the HO<sub>2</sub>-H<sub>2</sub>O adduct.

In this paper the current recommendations for the kinetics of the HO<sub>2</sub> disproportionation reaction have been investigated and compared against a new scheme that implicitly accounts for the formation of HO<sub>2</sub>-H<sub>2</sub>O. Using this new scheme of reactions our numerical model results suggest that the flux of the HO<sub>2</sub> disproportionation reaction is currently underestimated by on average 16% over all RH leading to under prediction of mixing ratios of H<sub>2</sub>O<sub>2</sub> by up to 10% and over prediction of HO<sub>2</sub> by up to 12%. It is suggested that for detailed modelling studies concerning marine boundary layer type conditions that the adopted parameterisation for formation and reactions of HO<sub>2</sub>-H<sub>2</sub>O should be considered in favour of the current recommendations which do not fully describe the complexity of this reaction. The reaction of these HO<sub>2</sub>-H<sub>2</sub>O complexes with other peroxy radicals (RO<sub>2</sub>) would be an interesting set of reactions to investigate further. At the low NO<sub>x</sub> conditions explored in this study, they would be another important reaction partner.

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