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# Investigation of organic hydrotrioxide (ROOOH) formation from RO<sub>2</sub> + OH reactions and their atmospheric impact using a chemical transport model, STOCHEM-CRI†

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Incorporating the reactions of fifty peroxy radicals (RO<sub>2</sub>) with the hydroxyl radical (OH) into the global chemistry transport model, STOCHEM-CRI, affected the composition of the troposphere by changing the global burdens of NO<sub>x</sub> (−2.7 Gg, −0.5%), O<sub>3</sub> (−2.3 Tg, −0.7%), CO (−3.2 Tg, −0.8%), HO<sub>x</sub> (+2.1 Gg, +7.7%), H<sub>2</sub>O<sub>2</sub> (+0.5 Tg, +18.3%), RO<sub>2</sub> (−8.0 Gg, −18.2%), RONO<sub>2</sub> (−19.4 Gg, −4.7%), PAN (−0.1 Tg, −3.4%) HNO<sub>3</sub> (−7.4 Gg, −1.3%) and ROOH (−96.9 Gg, −3.8%). The RO<sub>2</sub> + OH addition reactions have a significant impact on HO<sub>2</sub> mixing ratios in tropical regions with up to a 25% increase, resulting in increasing H<sub>2</sub>O<sub>2</sub> mixing ratios by up to 50% over oceans. Globally, a significant amount of organic hydrotrioxides (ROOOH) (86.1 Tg per year) are produced from these reactions with CH<sub>3</sub>OOOH (67.5 Tg per year, 78%), isoprene-derived ROOOH (5.5 Tg per year, 6%) and monoterpene-derived ROOOH (4.2 Tg per year, 5%) being the most significant contributors. The tropospheric global burden of CH<sub>3</sub>OOOH is found to be 0.48 Gg. The highest mixing ratios of ROOOH, of up to 0.35 ppt, are found primarily in the oceans near the tropical land areas. The RO<sub>2</sub> + OH reactions have a small, but noticeable, contribution to OH reactivity (~5%) over tropical oceans. Additionally, these reactions have a significant impact on RO<sub>2</sub> reactivity over tropical oceans where losses of the CH<sub>3</sub>O<sub>2</sub> radical, isoprene derived peroxy radical (ISOPO<sub>2</sub>) and monoterpene derived peroxy radical (MONOTERPO<sub>2</sub>) by OH can contribute up to 25%, 15% and 50% to the total RO<sub>2</sub> loss, respectively. The changes in RO<sub>2</sub> reactivity influence the global abundances of organic alcohols (ROH) which are important species due to their crucial impact on air quality. The ROOOH generate secondary organic aerosol (SOA) of up to 0.05 μg m<sup>−3</sup> which affects the Earth's radiation budget because of enhancing modelled organic aerosol by up to 5% and 2000% on land surfaces and the remote tropical oceans, respectively.

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## Environmental significance

Organic hydrotrioxides (ROOOH) formed from the oxidation of peroxy radicals (RO<sub>2</sub>) by OH in the troposphere play a significant role in the oxidising capacity of the atmosphere. Investigation of RO<sub>2</sub> + OH reactions and their product distributions is important for understanding the impact of volatile organic compound (VOC) emission and their chemistry that degrades air quality in the troposphere. In this study, we quantify the production of ROOOH from both anthropogenic and biogenic VOCs and their role in secondary organic aerosol formation. The inclusion of RO<sub>2</sub> + OH reactions in global Chemistry Transport Models (CTMs) and Earth System Models (ESMs) is highly recommended for the assessment of policies addressing global air quality and climate change.

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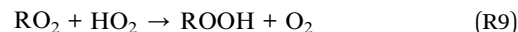
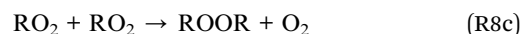
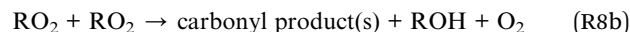
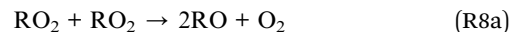
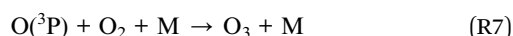
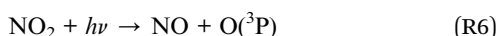
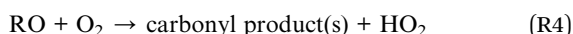
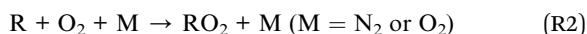
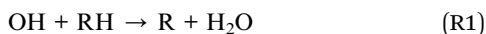
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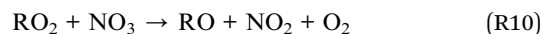


# 1. Introduction

Organic peroxy radicals ( $\text{RO}_2$ ) are highly reactive intermediates and are ubiquitous in the troposphere.<sup>1–6</sup> They are mainly formed from the oxidation of volatile organic compounds (VOCs) by hydroxyl radicals ( $\text{OH}$ ) *via* reactions (R1) and (R2) and additionally by ozone ( $\text{O}_3$ ), nitrate radicals ( $\text{NO}_3$ ), stabilized Criegee intermediates (SCIs) and chlorine atoms ( $\text{Cl}$ ).  $\text{RO}_2$  can be lost by several gas phase reactions depending on the nature of the tropospheric chemistry regime, whether it is low  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) ( $\text{NO}$  mixing ratios typically smaller than 10 pptv) or high  $\text{NO}_x$  ( $\text{NO}$  mixing ratios typically higher than 1 ppbv). In high  $\text{NO}_x$  environments, the dominant loss of tropospheric  $\text{RO}_2$  is through reaction with nitric oxide ( $\text{NO}$ ) which produces an alkoxy radical ( $\text{RO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ), leading to  $\text{HO}_x$  ( $= \text{OH} + \text{HO}_2$ ) propagation and  $\text{NO}_x$  catalysed ozone generation ( $\text{O}_3$ ) (R3a–R7).<sup>3,4,7,8</sup> A small branching ratio exists for the reaction between  $\text{RO}_2$  and  $\text{NO}$  (R3b) resulting in the formation of organic nitrates ( $\text{RONO}_2$ ). The yields of ozone and  $\text{RONO}_2$  strongly depend on the composition of VOCs and the amount of oxidants ( $\text{OH}$ ,  $\text{O}_3$ ,  $\text{Cl}$ , SCIs or  $\text{NO}_3$ ) in the atmosphere.<sup>9–11</sup> However, in low  $\text{NO}_x$  environments,  $\text{RO}_2$  radicals preferentially react with other  $\text{RO}_2$ , including hydroperoxy radicals ( $\text{HO}_2$ ),<sup>5</sup> or isomerise or auto-oxidise to form different multi-functionalised oxygenated peroxy radicals.<sup>12</sup> The highly oxygenated organic molecules (HOM) formed from the isomerisation or auto-oxidation of  $\text{RO}_2$  can condense on pre-existing particles and contribute to the formation of secondary organic aerosol (SOA).<sup>13</sup> The peroxy–peroxy radical self- and cross-reactions lead to either formation of  $\text{RO}$  (R8a) or a chain terminating mechanism that ultimately results in carbonyl and alcohol production (R8b) or formation of dimers.<sup>4,14</sup> The extent of the branching of this reaction is determined by the nature of the alkyl group incorporated into the  $\text{RO}_2$  radical.<sup>3,5</sup> The  $\text{RO}$  formed predominantly from  $<\text{C}_5$  peroxy radicals proceed to react with  $\text{O}_2$  yielding  $\text{HO}_2$  which can go on to participate in a further reaction with  $\text{RO}_2$  ((R4) and (R9)) to form organic hydroperoxides ( $\text{ROOH}$ ).  $\text{ROOH}$  act as temporary  $\text{HO}_x$  reservoirs until they are subjected to photolysis or undergo reaction with  $\text{OH}$ .  $\text{ROOH}$  can also be lost from the troposphere *via* deposition as well as participating in the formation of SOA.<sup>15–20</sup>

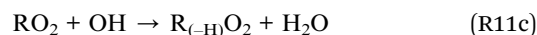
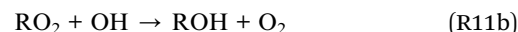


The rates at which  $\text{RO}_2$  react are directly related to their structure and the nature of their organic moiety.  $\text{RO}_2$  self-reactions act to slow the production of  $\text{O}_3$  from  $\text{RO}_2$ , and, in some circumstances,  $\text{O}_3$  formation is eliminated completely if the rate of the self-reaction is fast.<sup>21</sup> At night-time, the reaction between  $\text{RO}_2$  and  $\text{NO}_3$  is important which increases the concentrations of  $\text{RO}$  and  $\text{HO}_x$  *via* propagation reactions ((R10) and (R4)).<sup>2,22</sup>



Experimental studies have shown that  $\text{CH}_3\text{O}_2$  reacts rapidly with  $\text{OH}$  with a range of rate coefficients *e.g.*,  $2.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>23</sup>  $8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>24</sup>  $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>25</sup> and  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>26</sup> The reactions of larger peroxy radicals,  $\text{RO}_2$  ( $\text{C}_2\text{H}_5\text{O}_2$  to  $\text{C}_4\text{H}_9\text{O}_2$ ) with  $\text{OH}$  showed the same behaviour but with larger rate constants *e.g.*  $1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>27,28</sup> Large rate coefficients are also reported by Berndt *et al.*<sup>29</sup> for the reactions of isoprene and monoterpene derived peroxy radicals with  $\text{OH}$ , *e.g.*  $5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\text{HO-C}_5\text{H}_8\text{O}_2$ ,  $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\text{HO-C}_5\text{H}_8(\text{O})_2$  and  $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $\text{HO-C}_{10}\text{H}_{16}(\text{O})_2\text{O}_2$ . So, the  $\text{RO}_2 + \text{OH}$  reactions are competitive with reactions (R3), (R8) and (R10) and act as major sinks for  $\text{RO}_2$  in remote atmospheres.

The possible products of the  $\text{RO}_2 + \text{OH}$  reactions are as follows:



The estimation through theoretical approaches by Müller *et al.*<sup>30</sup> and through experiments by Yan *et al.*<sup>24</sup> and Assaf *et al.*<sup>27</sup> showed a negligible product, SCI (R11c) with a fractional upper limit of 0.05 and different branching ratios for reaction (R11a) and (R11b) if  $\text{R}=\text{CH}_3$ . An experimental kinetic study of the reaction of  $\text{CH}_3\text{O}_2 + \text{OH}$  by Caravan *et al.*<sup>31</sup> suggested that channel (R11b) is an insignificant product channel with yields of 0.09 and 0.06 at low and high pressure, respectively. A high yield of 0.9 for reaction (R11a) was determined experimentally at low pressure (67 hPa),<sup>32</sup> which is consistent with the best theoretical estimate (0.92) determined by Müller *et al.*<sup>30</sup> The yield for reaction (R11a) is highly dependent on the size of  $\text{RO}_2$  and is reduced to 0.75 for  $\text{C}_2\text{H}_5\text{O}_2$ , 0.41 for  $\text{C}_3\text{H}_7\text{O}_2$  and 0.15 for



$C_4H_9O_2$ .<sup>32</sup> The decrease of the yield of reaction (R11a) with increasing size of the R group led to the increase of the stabilization of ROOOH (R11d).<sup>29</sup> Müller *et al.*<sup>30</sup> predicted a yield for stabilized trioxide ( $CH_3OOOH$ ) (R11d) of 0.07 at 760 torr. However, with increasing the size of the R, the formation of thermalized ROOOH is the dominant product from (R11).<sup>29</sup> The ROOOH formed in (R11d) have several possible fates, among which are reaction with OH and uptake by aqueous aerosols followed by decomposition into ROH +  $O_2$  which could be the dominant channel.<sup>30</sup>

The reaction of  $RO_2$  with NO and  $HO_2$  and self- or cross-reactions with other  $RO_2$  radicals are included in most of the atmospheric chemistry transport models (CTMs), but  $RO_2$  + OH reactions are not explicitly considered in CTMs yet because of unexplored rate coefficients of the reaction of large  $RO_2$  radicals with OH, the yields of the products and the fate of the ROOOH formed from these reactions. We considered all  $RO_2$  + OH reactions taking into account the literature-based rate coefficients and product yields for channels (R11a–R11d) which led to an update of the burdens of the global tropospheric composition and their life cycles. Taking into account the lack of global modelling studies of  $RO_2$  with OH radicals and their potential impact in low  $NO_x$  environments, we have incorporated these reactions in the STOCHEM-CRI model and investigated the impact of these reactions on tropospheric composition. The formation of individual ROOOH, their distribution throughout the troposphere and their environmental impacts in terms of SOA formation have been investigated in the study. We also showed the impact of  $RO_2$  + OH reactions on the loss rates of peroxy radicals and hydroxyl radicals focusing on the tropics and discussed their implications for the oxidising capacity of the atmosphere.

## 2. Model description

STOCHEM is a global three-dimensional transport model that utilises a 3-hour time step for the advection of its 50 000 constant mass air parcels that represent the Earth's troposphere.<sup>33</sup> It is within these air parcels that the chemical reactions and photochemical dissociations leading to the loss and production of trace gases are taking place. The data concerning pressure, temperatures, winds, clouds, humidities, tropopause heights, precipitation, boundary layer depth and surface parameters are taken for the year 1998 from archived meteorological data from the UKMO Unified Model (UM).<sup>34</sup> Meteorological data are based on a grid resolution of  $1.25^\circ$  longitude,  $0.833^\circ$  latitude and 12 unevenly spaced (with respect to altitude) vertical levels between the surface and an upper boundary of  $\sim 100$  mb.<sup>33</sup> A Lagrangian approach for advection allows uncoupling of the chemistry and transport processes. The chemical mechanism used in STOCHEM is the Common Representative Intermediates (CRI) version 2 reduction 5 (CRI v2-R5) which was built using a series of five-day box model simulations on each compound, on a compound-by-compound basis. CRI v2-R5 was developed initially by Jenkin *et al.*<sup>35</sup> from the Master Chemical Mechanism (<https://mcm.york.ac.uk/MCM/>) with subsequent improvement by Watson *et al.*,<sup>36</sup> and

the CRI scheme involves the most reduced mechanism, making it suitable for global modelling due to its traceability to the MCM. More details of the CRI v2-R5 mechanism can be found in Utembe *et al.*<sup>37,38</sup> and recent updates of the CRI v2.2 mechanism can be found in Jenkin *et al.*<sup>39</sup> STOCHEM-CRI calculates one-hourly photolysis rates for each reaction within each air parcel, before linearly interpolating the data with respect to time. This provides photolysis rates at a resolution of 5 minutes to be used in the chemical integration. The photolysis rates were calculated by integrating (over all wavelengths) the product of flux, absorption cross section and quantum yield<sup>33</sup> which were included in the model as described in Khan *et al.*<sup>40</sup> In addition to the gas phase chemical reaction and photolysis, the air parcels are also influenced by emissions and physical removal processes (dry and wet deposition). The prevalent physical removal processes for chemical species within air parcels within the boundary layer are dry deposition and wet deposition. Dry deposition rates depend on whether a Lagrangian air parcel is over land or ocean with appropriate species dependent deposition velocities. The dry deposition velocities used in STOCHEM were adapted from the annual mean values calculated using the MATCH global model.<sup>41</sup> The removal of soluble species through dissolution in precipitation is known as wet deposition. These dissolved components can originate in the environment during cloud activation or incorporate into precipitation as it falls. The scavenging coefficients for convective and dynamic precipitation taken from Penner *et al.*<sup>42</sup> were combined with precipitation rates and scavenging profiles to calculate the loss rates of species (wet deposition) from an air parcel.

Emissions are treated as an additional term to the source fluxes of each species during each integration time step.<sup>33,43</sup> The emission profile for STOCHEM-CRI consists of three different categories: surface emissions, stratospheric sources and 3-dimensional emissions. Emissions that fall under surface emissions are anthropogenic, biomass burning, oceans, soils and vegetation which are mapped monthly from a two-dimensional source map at a resolution of  $5^\circ$  longitude  $\times$   $5^\circ$  latitude. The emission data employed in the base case STOCHEM-CRI model were adapted from the Precursor of Ozone and their Effects in the Troposphere (POET) inventory for the year 1998.<sup>44</sup> More details about the emission data can be found in Khan *et al.*<sup>45</sup> The emissions flux is implemented during the chemical timestep unless there are no Lagrangian cells present in a particular Eulerian grid cell, in which case the emissions are stored for implementation after the next advection step. Finally, all emissions are converted into units of molecules per second per grid square.

In this study, the base case experiment involves the STOCHEM being integrated with the CRI v2-R5 mechanism with the updated isoprene  $HO_x$  recycling mechanism<sup>46</sup> subsequently referred to as 'STOCH-base'. A further simulation, 'STOCH- $RO_2$ -OH' was performed which involved the inclusion of all organic peroxy radicals ( $RO_2$ ) + OH reactions, with product yields of reaction weighted averages across different  $RO_2$  of 0.82, 0.07, 0.0, 0.11 for channels (R11a–R11d), respectively for each individual reaction to the STOCH-base scenario. A total of 200



reactions for 50 RO<sub>2</sub> species are thus added in STOCHEM-RO<sub>2</sub>-OH. The rate coefficients of RO<sub>2</sub> + OH reactions show no significant dependence on the size of the R group on the RO<sub>2</sub>, thus all  $k_{\text{OH}+\text{RO}_2}$  were assumed to be  $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 295 K which was selected on the basis of the experimental determination for the CH<sub>3</sub>O<sub>2</sub> + OH reaction from the work of Assaf *et al.*<sup>25</sup> The products of (R11a) are based on similar alkoxy radical formation as in the reactions of RO<sub>2</sub> + NO already in the CRI mechanism. The unique products from the reactions (R11b–R11d) are considered as ROH, R<sub>(-H)</sub>OO and ROOOH. The loss of ROOOH to ROH + O<sub>2</sub> with a rate coefficient of  $5.0 \times 10^{-3} \text{ s}^{-1}$  was used which was estimated based on the studies of Müller *et al.*<sup>30</sup> and Caravan *et al.*<sup>31</sup> The losses of ROH and R<sub>(-H)</sub>OO were considered in the model based on the loss processes of C<sub>3</sub>H<sub>8</sub>OH and CH<sub>3</sub>CHOO already in the CRI mechanism, respectively. As the product yields of (R11) are highly variable with the size of the alkyl moiety of the peroxy radicals, we performed four further model simulations assuming 100% yield for each individual channel (R11a–R11d) referred to as STOCH-RO<sub>2</sub>-OH-A, STOCH-RO<sub>2</sub>-OH-B, STOCH-RO<sub>2</sub>-OH-C, and STOCH-RO<sub>2</sub>-OH-D, respectively. Another simulation, STOCH-CH<sub>3</sub>O<sub>2</sub>-OH, was performed including only the reaction of CH<sub>3</sub>O<sub>2</sub> + OH to assess the impact of the reaction on the global budget of CH<sub>3</sub>OH and CH<sub>3</sub>OOOH. All simulations were conducted with meteorology from 1998 for a period of 24 months with the first 12 allowing the model to spin up. Analyses were performed on the subsequent 12 months of data. Using the loss of OH by RO<sub>2</sub> and loss of RO<sub>2</sub> by OH derived from the STOCH-RO<sub>2</sub>-OH model run for each model box in the tropical region, we calculated the fraction of this loss process compared with the total OH and RO<sub>2</sub> losses. Formation of SOA from ROOOH is accounted for in the model by equilibrium partitioning between gas and aerosol phases, based on the Pankow absorption model.<sup>47</sup> The vapor pressures of all ROOOH were calculated using the method of Nannoolal *et al.*<sup>48</sup> in conjunction with species boiling points estimated by the method of Nannoolal *et al.*<sup>49</sup> extracted directly from the University of Manchester multiphase system online property prediction (UManSysProp) facility.<sup>50</sup> The method employed in the model to account for the partitioning of the gas-phase insertion products onto pre-

existing primary organic aerosol has been documented previously.<sup>17,18</sup> Nine ROOOH (RTN28OOOH, RTN26OOOH, RTN25OOOH, RTN24OOOH, RTN23OOOH, RTN14OOOH, RTX28OOOH, RU12OOOH, and NRU12OOOH) showed sufficiently low volatilities and a similar technique<sup>17</sup> is utilised in this study to account for their role as nucleating agents for new particle formation.

### 3. Results and discussion

#### 3.1. Impact of (R11) on the global burden of the species

The STOCHEM-RO<sub>2</sub>-OH model simulation results show that a significant amount of ROOOH (86.1 Tg per year) and ROH (30.2 Tg per year from direct reaction of (R11b) and 47.5 Tg per year through ROOOH decomposition) was formed from RO<sub>2</sub> + OH reactions (Table 1 and ESI Table S1†). Among all ROOOH and ROH, the formation of CH<sub>3</sub>OOOH (67.5 Tg per year, 78%) and CH<sub>3</sub>OH (55.2 Tg per year, 71%) is found to be the highest. In a previous study utilising the same model, we reported a global budget of CH<sub>3</sub>OH by photochemical production of 48 Tg per year through the reaction of CH<sub>3</sub>O<sub>2</sub> + RO<sub>2</sub>.<sup>45</sup> In the STOCHEM-RO<sub>2</sub>-OH model, we found ~50% decreased CH<sub>3</sub>OH production from CH<sub>3</sub>O<sub>2</sub> + RO<sub>2</sub> (23.5 Tg per year) similar to the study of Bates *et al.*<sup>51</sup> (24.0 Tg per year). However, we also found a total secondary methanol production of 78.7 Tg per year, which is ~60% and ~30% higher than that reported by Khan *et al.*<sup>45</sup> and Bates *et al.*,<sup>51</sup> respectively. The reduction in CH<sub>3</sub>O<sub>2</sub> due to its reaction with OH retarded the *in situ* production of CH<sub>3</sub>OH through the self-reaction of CH<sub>3</sub>O<sub>2</sub> and its cross-reactions with other RO<sub>2</sub> resulting in decreasing methanol production from CH<sub>3</sub>O<sub>2</sub> + RO<sub>2</sub>.<sup>31</sup> In the STOCHEM-RO<sub>2</sub>-OH model, the CH<sub>3</sub>O<sub>2</sub> + OH reaction directly produced 21.5 Tg per year CH<sub>3</sub>OH and 67.5 Tg per year CH<sub>3</sub>OOOH formation followed by its decomposition to produce further 33.7 Tg per year CH<sub>3</sub>OH. In contrast, the study of Bates and co-workers<sup>51</sup> considered only the primary formation of CH<sub>3</sub>OH (33 Tg per year) with a yield of 13% and did not consider the secondary formation *via* CH<sub>3</sub>OOOH. From the STOCH-CH<sub>3</sub>O<sub>2</sub>-OH model simulation results, the global burdens were found to be 5.56 Tg for CH<sub>3</sub>OH and 0.48 Gg for CH<sub>3</sub>OOOH. The atmospheric

Table 1 Contribution of different ROOOH and ROH from STOCHEM-RO<sub>2</sub>-OH model simulation

| ROOOH/ROH <sup>a</sup>                    | Total number of species | Formation of ROOOH (Tg per year) | Formation of ROH (Tg per year) |
|-------------------------------------------|-------------------------|----------------------------------|--------------------------------|
| CH <sub>3</sub> OOOH/CH <sub>3</sub> OH   | 1                       | 67.5                             | 55.2                           |
| Small specific ROOOH/ROH <sup>b</sup>     | 6                       | 1.9                              | 2.0                            |
| Isoprene derived ROOOH/ROH <sup>c</sup>   | 7                       | 5.5                              | 7.0                            |
| α,β-Pinene derived ROOOH/ROH <sup>d</sup> | 12                      | 4.2                              | 5.8                            |
| RC(O)OOOH/RC(O)OH <sup>e</sup>            | 4                       | 5.4                              | 5.9                            |
| Other ROOOH/ROH <sup>f</sup>              | 20                      | 1.6                              | 1.8                            |
| Total ROOOH/ROH                           | 50                      | 86.1                             | 77.7                           |

<sup>a</sup> Structures can be obtained using the species name and search facility on the MCM website (<https://mcm.york.ac.uk/MCM/>). <sup>b</sup> Small ROOOH/ROH species are specific C1–C3 structures that are derived from degradation of many VOCs. <sup>c</sup> ROOOH/ROH species are derived solely from isoprene degradation. <sup>d</sup> ROOOH/ROH species are derived solely from monoterpene (α-pinene and β-pinene) degradation. <sup>e</sup> Small RC(O)OOOH/RC(O)OH species are derived from degradation of many VOCs. <sup>f</sup> Other ROOOH/ROH species are derived from degradation of all other VOCs. More detailed information about individual contributions of ROOOH and ROH can be found in ESI Table S1.





lifetime of  $\text{CH}_3\text{OH}$  was found to be 6.8 days for  $\text{CH}_3\text{OH}$ , which was within the range of the estimated lifetime by Jacob *et al.*<sup>52</sup> After  $\text{CH}_3\text{OOH}$  and  $\text{CH}_3\text{OH}$ , isoprene-derived  $\text{ROOOH}$  (5.5 Tg per year, 6%) and  $\text{ROH}$  (7.0 Tg per year, 9%), monoterpene-derived  $\text{ROOOH}$  (4.2 Tg per year, 5%) and  $\text{ROH}$  (5.8 Tg per year, 7%), peroxy acetyl- $\text{OOH}$  (5.4 Tg per year, 6%) and peroxy acetyl- $\text{OH}$  (5.9 Tg per year, 8%) made up the most significant contributions to the total formation of  $\text{ROOOH}$  and  $\text{ROH}$ , respectively (Table 1). The isoprene and monoterpene derived  $\text{ROH}$  and  $\text{ROOOH}$  in the model were highly oxidized molecules and have a significant impact on SOA, which will be discussed in more detail in Section 3.5.

The detailed summary of the atmospheric composition simulated under the STOCH-base case and the changes resulting under the STOCH- $\text{RO}_2$ -OH scenario are shown in Table 2. The inclusion of the fifty  $\text{RO}_2 + \text{OH}$  reactions in the STOCH- $\text{RO}_2$ -OH resulted in little change to the global burdens of  $\text{NO}_x$  (−2.65 Gg, −0.5%),  $\text{O}_3$  (−2.3 Tg, −0.7%),  $\text{CO}$  (−3.2 Tg, −0.8%),  $\text{CH}_3\text{CHO}$  (+2.1 Gg, +1.4%) and  $\text{HNO}_3$  (−7.4 Gg, −1.3%). However, compared with the STOCH-base case, the  $\text{RO}_2 + \text{OH}$  reactions have significant impacts on the global trace gas burdens with increments of 2.1 Gg  $\text{HO}_x$  (7.7%) and 0.53 Tg  $\text{H}_2\text{O}_2$  (18.3%) and decrements of 8.0 Gg  $\text{RO}_2$  (18.2%), 19.4 Gg  $\text{RONO}_2$  (4.7%), 0.11 Tg PAN (3.4%), 34.9 Gg  $\text{HCHO}$  (3.3%) and 96.6 Gg  $\text{ROOH}$  (3.8%).

Our previous study of the atmospheric impact of the  $\text{CH}_3\text{O}_2 + \text{OH}$  reaction<sup>31</sup> showed that the reaction of methyl peroxy and hydroxyl radicals increased the global burden of  $\text{HO}_x$  by 6.2%. The inclusion of all fifty  $\text{RO}_2 + \text{OH}$  reactions in this study increased the global burden of  $\text{HO}_x$  by 7.7%. These reactions proceed through oxygen atom transfer from  $\text{RO}_2$  to OH producing  $\text{HO}_2$ , hence the large production of  $\text{HO}_2$  (569.6 Tg per year) and the significant loss of OH (186.4 Tg per year) from these reactions found in the STOCH- $\text{RO}_2$ -OH simulation. The burden change of  $\text{HO}_x$  ( $=\text{OH} + \text{HO}_2$ ) was a balance between two opposite effects; however, the production of  $\text{HO}_2$  was outweighed by the loss of OH resulting in an increase in the global

burden of  $\text{HO}_x$ .  $\text{H}_2\text{O}_2$  acts a reservoir of  $\text{HO}_x$ ; thus the annual mean global burden of  $\text{H}_2\text{O}_2$  is increased by 534.2 Gg (18.3%) due to the increased  $\text{H}_2\text{O}_2$  production (132.2 Tg per year, 18.2% from the STOCH-base case) from the  $\text{HO}_2 + \text{HO}_2$  reaction.  $\text{ROOH}$  was another reservoir of  $\text{HO}_x$ , but the global burden of  $\text{ROOH}$  is decreased by 96.6 Gg (3.8%) due to its reduced production (444.3 Tg per year, 13.9%) from the  $\text{RO}_2 + \text{HO}_2$  reaction following on from the decreased  $\text{RO}_2$  level. Due to the increase of  $\text{HO}_2$  burden in the STOCH- $\text{RO}_2$ -OH, the production of ozone through  $\text{HO}_2 + \text{NO}$  was increased by 319.5 Tg per year (7.8%). However, the decreased levels of  $\text{RO}_2$  have the effect of decreasing the production of ozone through the  $\text{RO}_2 + \text{NO}$  channel by 325.8 Tg per year (10.0%). In addition, the increased  $\text{HO}_2$  enhanced the loss of ozone through the  $\text{HO}_2 + \text{O}_3$  reaction by 68.7 Tg per year (5.7%). Overall, the ozone burden decreased by 2.3 Tg (0.7%). The decreased production of  $\text{NO}_2$  through the  $\text{RO}_2 + \text{NO}$  reaction had the effect of decreasing the tropospheric burden of  $\text{NO}_x$  (2.7 Gg, 0.5%). The combined effect of decreased  $\text{RO}_2$  and decreased  $\text{NO}_x$  also resulted in lower productions of related  $\text{NO}_x$  oxidation products, as the global burden of  $\text{RONO}_2$  and PAN decreased by 19.4 and 112.9 Gg, respectively. Additionally, the  $\text{HNO}_3$  global burden was decreased by 7.4 Gg (1.5%) due to its decreased production (4.5 Tg per year, 2.3%) through the  $\text{OH} + \text{NO}_2$  reaction. Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and formaldehyde ( $\text{HCHO}$ ) are oxidation products of VOCs, including  $\text{RO}_2$  and  $\text{ROOH}$ . Hence, the decreased levels of  $\text{RO}_2$  and  $\text{ROOH}$  in STOCH- $\text{RO}_2$ -OH produced smaller amounts of  $\text{HCHO}$  (337.2 Tg per year) and  $\text{CH}_3\text{CHO}$  (6.8 Tg per year). However, the oxidation of  $\text{RO}_2$  with OH produced additional amounts of  $\text{HCHO}$  (244.5 Tg per year) and  $\text{CH}_3\text{CHO}$  (6.9 Tg per year). Overall, the global burden of  $\text{HCHO}$  decreased by 30.5 Gg (2.9%) and the global burden of  $\text{CH}_3\text{CHO}$  increased by 0.87 Gg (0.2%), respectively.

### 3.2. Impact of (R11) on the surface distribution of the species

The percentage change in annual surface levels of OH,  $\text{HO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HCHO}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{RO}_2$ ,  $\text{ROOH}$ ,  $\text{NO}_x$ ,  $\text{HNO}_3$ , PAN and  $\text{RONO}_2$  in STOCH- $\text{RO}_2$ -OH compared with the STOCH-base case is shown in Fig. 1. The addition of fifty  $\text{RO}_2 + \text{OH}$  reactions had an impact on OH and  $\text{HO}_2$  mixing ratios near the equatorial region with up to 12% decrease and 25% increase over the oceans, respectively.  $\text{HO}_2$  and  $\text{RO}_2$  are important during the daytime and are produced during the oxidation of trace gases. In the equatorial regions, the abundances of these  $\text{RO}_2$  species are high due to the increased levels of VOCs along with increased photochemistry. When these  $\text{RO}_2$  radicals reacted with OH, the mixing ratios of  $\text{RO}_2$  radicals were reduced (by up to 50%). However, these  $\text{RO}_2$  produced a significant amount of  $\text{HO}_2$ , with a similar distribution to the decrease in  $\text{RO}_2$  in these regions (see Fig. 1). The inclusion of these reactions in the model led to an increase of  $\text{H}_2\text{O}_2$  mixing ratios by up to 50%. The significant increase of  $\text{H}_2\text{O}_2$  can enhance particle growth due to the increased oxidation of  $\text{SO}_2$  in cloud droplets formed on sulfuric acid seed aerosol.<sup>53</sup> The change of surface distribution of  $\text{H}_2\text{O}_2$  is driven by the increase in  $\text{HO}_2$  abundances (see

**Table 2** Global annual mean tropospheric burden of selected species for the STOCH-base case and the change of annual global burden for the STOCH- $\text{RO}_2$ -OH case<sup>a</sup>

| Species                 | Base global burden (Gg) | Change in global burden (Gg) |
|-------------------------|-------------------------|------------------------------|
| $\text{HO}_x$           | 26.7                    | +2.1 (+7.7)                  |
| $\text{O}_3$            | $310.8 \times 10^3$     | $-2.3 \times 10^3$ (−0.7)    |
| $\text{CO}$             | $401.2 \times 10^3$     | $-3.2 \times 10^3$ (−0.8)    |
| $\text{NO}_x$           | 492.2                   | −2.7 (−0.5)                  |
| $\text{H}_2\text{O}_2$  | $2.9 \times 10^3$       | +534.2 (+18.3)               |
| $\text{HCHO}$           | $1.1 \times 10^3$       | −34.9 (−3.3)                 |
| $\text{CH}_3\text{CHO}$ | 146.6                   | +2.1 (+1.4)                  |
| $\text{HNO}_3$          | 503.0                   | −7.4 (−1.5)                  |
| $\text{RONO}_2$         | 411.754                 | −19.4 (−4.7)                 |
| PAN                     | $3.3 \times 10^3$       | −112.9 (−3.4)                |
| $\text{RO}_2$           | 44.2                    | −8.0 (−18.2)                 |
| $\text{ROOH}$           | $2.5 \times 10^3$       | −96.6 (−3.8)                 |

<sup>a</sup> Global burdens are in Gg, percent changes are in brackets.



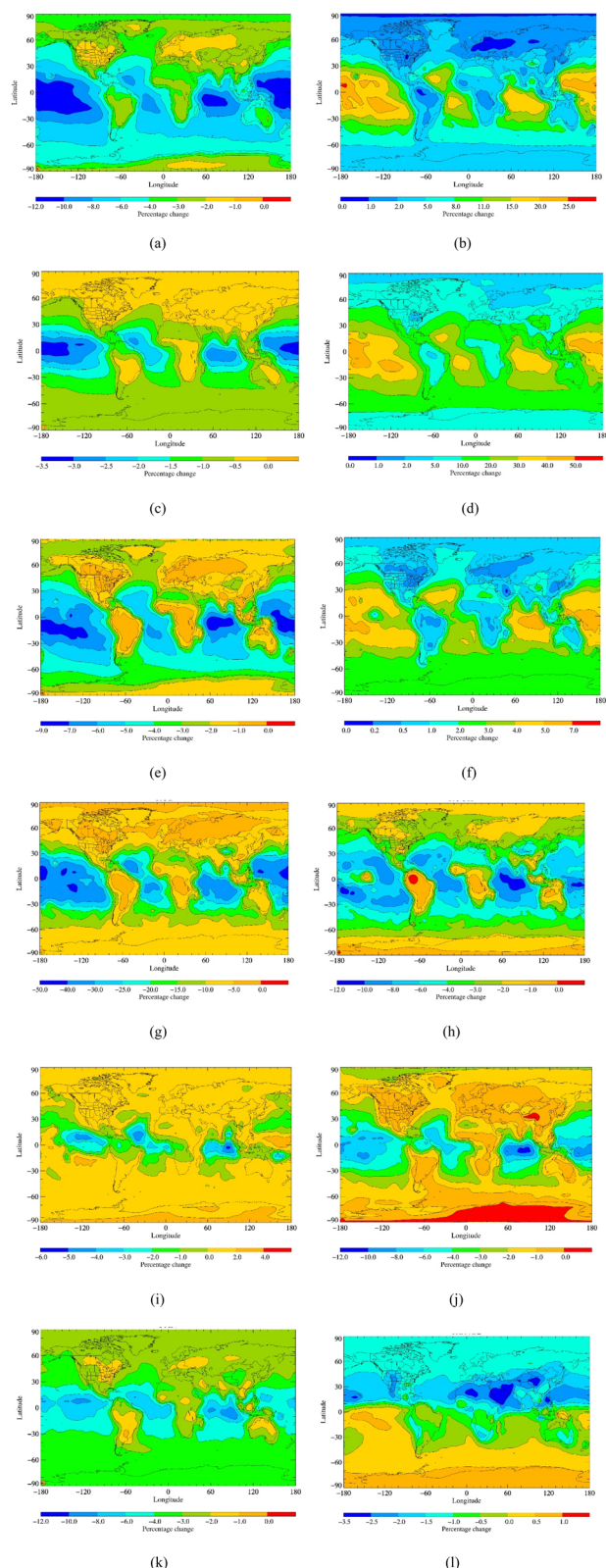


Fig. 1 Annual surface percentage changes in (a) OH, (b) HO<sub>2</sub>, (c) O<sub>3</sub>, (d) H<sub>2</sub>O<sub>2</sub>, (e) HCHO, (f) CH<sub>3</sub>CHO, (g) RO<sub>2</sub>, (h) ROOH, (i) NO<sub>x</sub>, (j) HNO<sub>3</sub>, (k) PAN and (l) RONO<sub>2</sub> on inclusion of RO<sub>2</sub> + OH reactions.

Fig. 1). The inclusion of RO<sub>2</sub> + OH reactions led to a decrease in NO<sub>x</sub> over tropical oceans by up to 6%. The decreased levels of NO<sub>x</sub> in the tropical ocean regions combined with decreased RO<sub>2</sub> resulted in the decreased formation of organic nitrates resulting in decreased PAN mixing ratios by up to 10% and decreased RONO<sub>2</sub> mixing ratios by up to 3.5% in the tropical ocean regions. A decrease in HNO<sub>3</sub> by up to 12% was also observed over the tropical oceans due to decreased levels of NO<sub>x</sub>. Over the oceans where NO<sub>x</sub> was decreased, the O<sub>3</sub> concentrations had decreased by up to 3.5% due to increased HO<sub>2</sub> levels.

The inclusion of the (R11) reaction set in the model produced up to 0.35 ppt ROOOH and an additional 150 ppt ROH in tropical regions. The spatial distributions of ROOOH and ROH mixing ratios were found to be similar to that of their precursors (OH and RO<sub>2</sub>). The highest mixing ratios of ROOOH were found mostly in the oceans adjacent to the tropical land areas, whereas the highest mixing ratios of ROH were found in the tropical forest regions (Fig. 2). The abundances of ROOOH in our study were found to be low compared with Fittschen *et al.*'s study<sup>54</sup> who used the UM-UKCA global chemistry-climate model with considering 100% yield of ROOOH from all RO<sub>2</sub> + OH reactions, using a low removal rate of ROOOH ( $1 \times 10^{-4} \text{ s}^{-1}$  compared with our study,  $5 \times 10^{-3} \text{ s}^{-1}$ ) and showing diurnal and seasonal peak concentrations of ROOOH in their calculation.

Caravan *et al.*<sup>31</sup> showed that CH<sub>3</sub>O<sub>2</sub> + OH is a significant source of CH<sub>3</sub>OH over the tropical ocean if the yield of ROH ( $\phi_{\text{ROH}}$ ) is higher than 0.15. In this study, we also found a significant increase of ROH over tropical regions using  $\phi_{\text{ROH}} = 0.18$  (direct (0.07) + through decomposition of ROOOH (0.11)). Excluding CH<sub>3</sub>O<sub>2</sub>, the biogenic RO<sub>2</sub> (especially isoprene derived peroxy radical (ISOPO<sub>2</sub>) and monoterpene derived peroxy radical (MONOTERPO<sub>2</sub>)) dominated over the tropical forest region; thus, the abundances of ROH were found to be highest in the tropical forest region.

### 3.3. Contribution of (R11) to the reactivity of OH and RO<sub>2</sub>

The RO<sub>2</sub> + OH addition reactions increase the OH reactivity by up to 5% over remote tropical oceans (Fig. 3a), consistent with the finding of Ferracci *et al.*<sup>55</sup> Considering the average loss fluxes of OH over the tropical region, it was found that RO<sub>2</sub> + OH reactions represented as much as  $0.05 \text{ s}^{-1}$  ( $\sim 2\%$  of the sinks) in the tropical regions (Fig. 3b and ESI Table S2†). This small OH reactivity contribution could not reduce the discrepancy of the model-measured OH reactivity with a mean bias of  $-11.9 \text{ s}^{-1}$  and  $-20.4 \text{ s}^{-1}$  for all locations and tropical regions, respectively (see ESI Table S3†). The significantly underestimated OH reactivity in the tropical forest area could be due to insufficient representation of reactive VOCs in the model, especially monoterpenes and sesquiterpenes.<sup>56</sup> No measurements have been performed so far in the tropical oceanic area on OH reactivity, so it was not possible to validate the improvement of the model-measured OH reactivity biases in the tropical oceans.

RO<sub>2</sub> + OH reactions enhanced CH<sub>3</sub>O<sub>2</sub>, ISOPO<sub>2</sub> and MONOTERPO<sub>2</sub> reactivities by up to 25%, 15% and 50%, respectively, over remote tropical oceans (Fig. 4a, 5a and 6a).

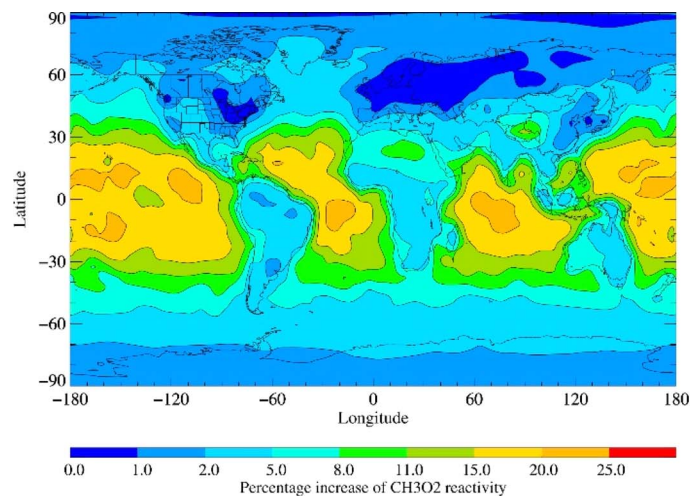




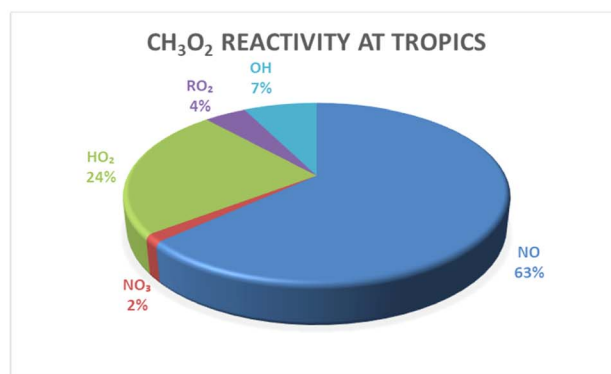
MONTERPO<sub>2</sub> + OH could be important for atmospheric aerosol formation and thus for the Earth's radiation budget.<sup>29</sup>

The STOCH-RO<sub>2</sub>-OH-A simulation results showed that the mixing ratios of HO<sub>2</sub> were further increased by up to 3.5% over remote oceans when the yield of (R11a) is increased from 0.82 to 1 (Fig. 7a). The yield increment of (R11a) did not have significant impacts (less than 1% change) on the mixing ratios of O<sub>3</sub>, OH, RO<sub>2</sub>, ROOH, RONO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>x</sub> and other species. The reasons for the small impact of these species were similar to the STOCH-RO<sub>2</sub>-OH simulation results explained in the previous



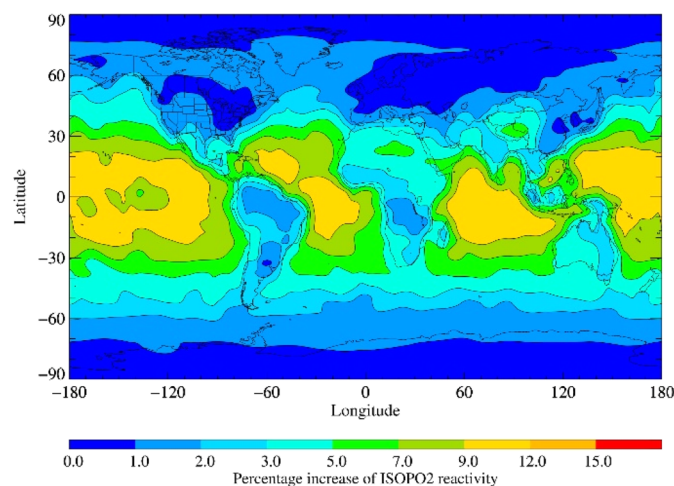


(a)

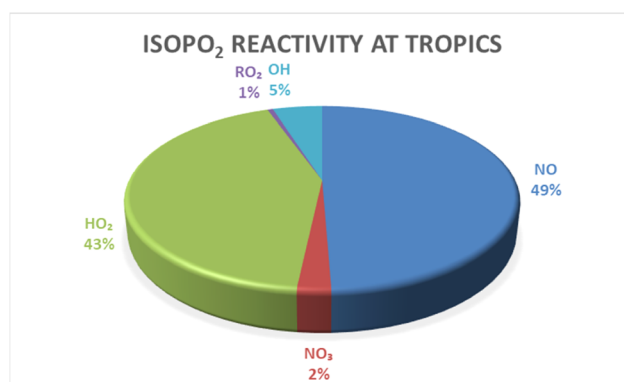


(b)

Fig. 4 (a) Percent increase in CH<sub>3</sub>O<sub>2</sub> reactivity on inclusion of RO<sub>2</sub> + OH reactions and (b) fraction of CH<sub>3</sub>O<sub>2</sub> reactivity over the tropical region.



(a)



(b)

Fig. 5 (a) Percent increase in ISOPO<sub>2</sub> reactivity on inclusion of RO<sub>2</sub> + OH reactions and (b) fraction of ISOPO<sub>2</sub> reactivity over the tropical region.

Section (3.2). The STOCH-RO<sub>2</sub>-OH-D simulation results showed significant amounts of ROOOH (up to 3 ppt; Fig. 7b) and ROH (up to 800 ppt; Fig. 7c) over tropical regions. The mixing ratios of ROH were found to be highest over tropical forest regions (*e.g.* Amazon and Congo) and the mixing ratios of ROOOH were found to be highest over the tropical oceans. The STOCH-RO<sub>2</sub>-OH-B simulation results also showed similar amounts (up to 800 ppt) and distribution of ROH (ESI Fig. S1a†) with a decrease of only 1% (~5 ppt, ESI Fig. S1b†) compared with the STOCH-RO<sub>2</sub>-OH-D simulation. Overall, the variation of the product yields from (R11b) and (R11d) does not have significant impact on ROH mixing ratios. The STOCH-RO<sub>2</sub>-OH-C simulation results showed that up to ~3000 molecules per cm<sup>3</sup> SCIs were

formed in the tropical oceanic regions (Fig. 7d). Experimental studies<sup>24,27</sup> suggest that this channel is negligible for R=CH<sub>3</sub>, however, for larger R, the scenario could be different. The STOCH-RO<sub>2</sub>-OH-C simulation produced ~1500 molecules per cm<sup>-3</sup> in the tropical forest region (Amazon) which added 8% to the total SCI concentrations.<sup>37</sup> However, the SCIs in the tropical oceans influenced the atmospheric oxidation capacity in the marine boundary layer significantly.

### 3.5. SOA formation from ROOOH

The STOCH-RO<sub>2</sub>-OH scenario (which includes the partitioning parameters of nine ROOOH) produced a non-negligible amount of SOA (up to 0.05 μg m<sup>-3</sup>, Fig. 8a) which can enhance model





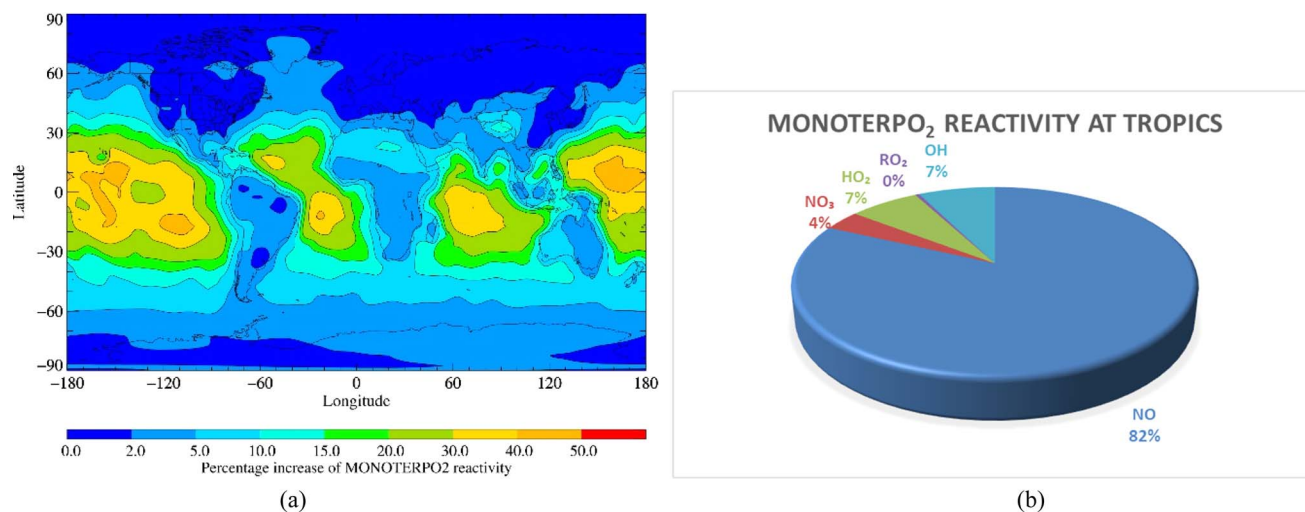


Fig. 6 (a) Percent increase in MONOTERPO<sub>2</sub> reactivity on inclusion of RO<sub>2</sub> + OH reactions and (b) fraction of MONOTERPO<sub>2</sub> reactivity over the tropical region.

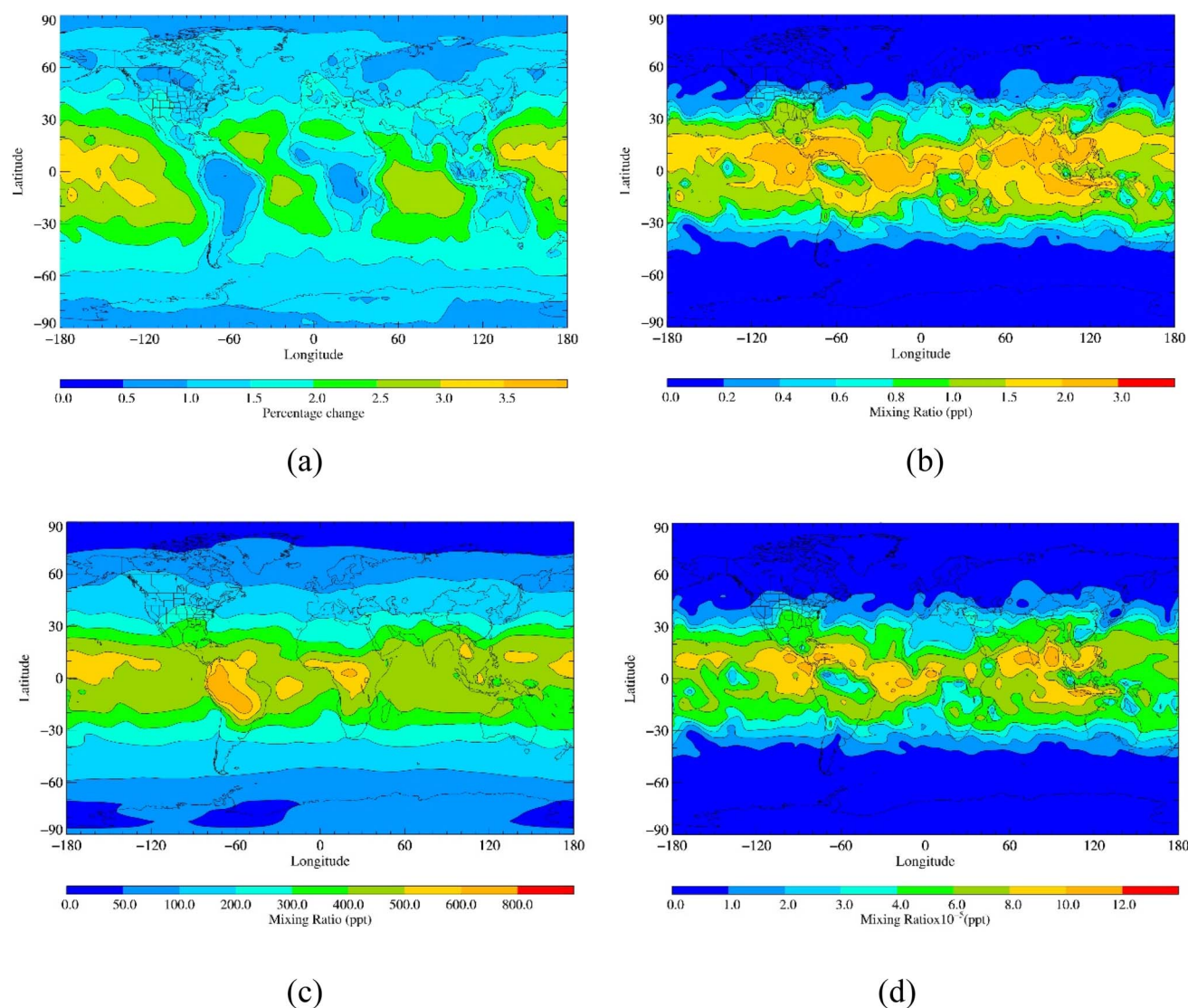


Fig. 7 (a) Annual HO mixing ratio change from STOCH-RO<sub>2</sub>-OH to STOCH-RO<sub>2</sub>-OH-A simulation, (b) annual ROOOH mixing ratios simulated by STOCH-RO<sub>2</sub>-OH-D, (c) annual ROH mixing ratios simulated by STOCH-RO<sub>2</sub>-OH-D, and (d) annual Criegee intermediate mixing ratios simulated by STOCH-RO<sub>2</sub>-OH-C.



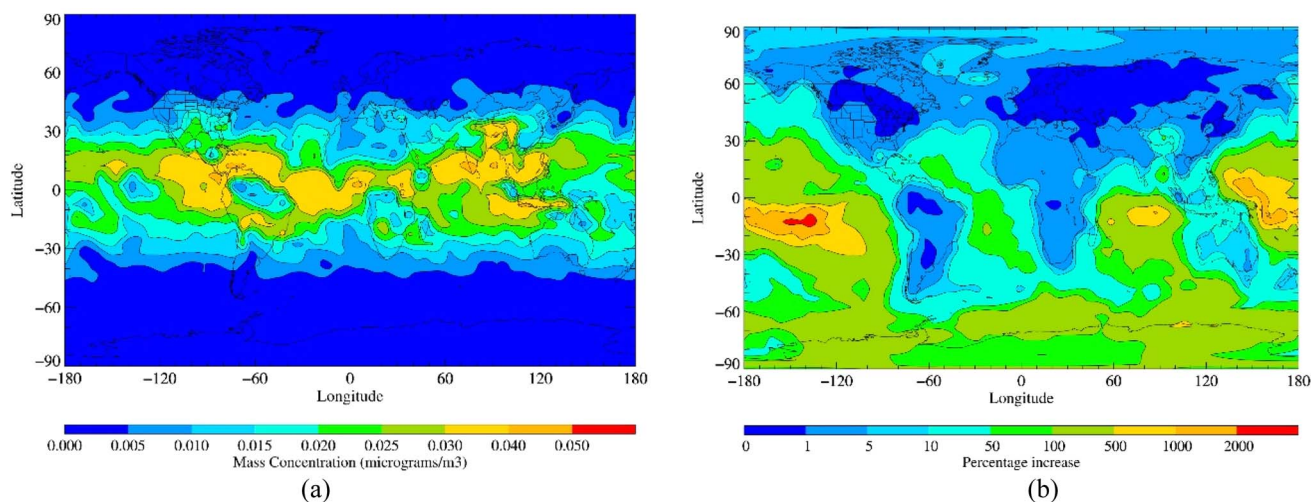


Fig. 8 (a) Annual SOA concentration simulated by STOCH-RO<sub>2</sub>-OH and (b) percentage annual increase of organic aerosol formation from STOCH-base.

organic aerosol by up to 5% on land surfaces (Fig. 8b). However, a significant enhancement (by up to 2000%) of organic aerosol was seen over the remote tropical oceans (Fig. 8b). When the partitioning parameters were included in the STOCH-RO<sub>2</sub>-OH-D model, the SOA formation was increased by up to 0.40  $\mu\text{g m}^{-3}$  ( $\sim 10$ -fold higher than STOCH-RO<sub>2</sub>-OH; ESI Fig. S2†). Currently, the STOCHEM-CRI model underpredicts organic aerosol mass concentration in remote, biomass burning, anthropogenically polluted and both biomass burning plume and anthropogenically polluted regions with mean biases of  $-0.26$ ,  $-1.69$ ,  $-2.03$  and  $-2.80$   $\mu\text{g m}^{-3}$ , respectively.<sup>18</sup> The SOA contribution from STOCH-RO<sub>2</sub>-OH and STOCH-RO<sub>2</sub>-OH-D simulations brought model into better agreement with observations, especially in remote regions with a bias reduction of  $-0.24$   $\mu\text{g m}^{-3}$  (7% improvement) and  $-0.10$   $\mu\text{g m}^{-3}$  (62% improvement), respectively (see ESI Fig. S3†).

## 4. Conclusion

Organic hydrotrioxides (ROOOH) are formed in the atmosphere through the gas-phase reaction of organic peroxy radicals (RO<sub>2</sub>) with hydroxyl radicals (OH). We simulated the reactions of RO<sub>2</sub> + OH with four different possible product channels and investigated the formation of ROOOH, their abundances and the environmental impacts in terms of secondary organic aerosol (SOA) formation. CH<sub>3</sub>OOOH (67.5 Tg per year, 78%) is the most significant contributor of ROOOH followed by isoprene-derived ROOOH (5.5 Tg per year, 6%), monoterpene-derived ROOOH (4.2 Tg per year, 5%) and peroxy acetyl-OOOH (5.4 Tg per year, 6%). The model simulations showed that the reactions of RO<sub>2</sub> by OH compete with their reactions by HO<sub>2</sub>, RO<sub>2</sub>, and NO<sub>x</sub> and change the global burdens of NO<sub>x</sub> ( $-2.65$  Gg,  $-0.5\%$ ), O<sub>3</sub> ( $-2.3$  Tg,  $-0.7\%$ ), CO ( $-3.2$  Tg,  $-0.8\%$ ), CH<sub>3</sub>CHO ( $+2.1$  Gg,  $+1.4\%$ ), HNO<sub>3</sub> ( $-7.4$  Gg,  $-1.3\%$ ), HO<sub>x</sub> ( $+2.1$  Gg,  $+7.7\%$ ) and 0.5 H<sub>2</sub>O<sub>2</sub> ( $+0.53$  Tg,  $+18.3\%$ ), RO<sub>2</sub> ( $-8$  Gg,  $-18.2\%$ ), RONO<sub>2</sub> ( $-19.4$  Gg,  $-4.7\%$ ), PAN ( $-0.11$  Tg,  $-3.4\%$ ), HCHO ( $-34.9$  Gg,  $-3.3\%$ ) and

ROOH ( $-96.9$  Gg,  $-3.8\%$ ). The surface RO<sub>2</sub> and HO<sub>2</sub> mixing ratios are found to be decreased by up to 50% and increased by up to 25%, respectively near the tropical oceanic region which are the important factors for changing the surface distribution of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HCHO, CH<sub>3</sub>CHO, RO<sub>2</sub>, ROOH, NO<sub>x</sub>, HNO<sub>3</sub>, PAN and RONO<sub>2</sub>. RO<sub>2</sub> + OH reactions represent as much as  $0.05$  s<sup>-1</sup> ( $\sim 2\%$  of the total OH sinks) in the tropical regions whereas CH<sub>3</sub>O<sub>2</sub> + OH, ISOPO<sub>2</sub> + OH and MONOTERPO<sub>2</sub> + OH reactions represent as much as  $3.7 \times 10^{-4}$  s<sup>-1</sup> ( $\sim 7\%$  of the total CH<sub>3</sub>O<sub>2</sub> sinks),  $2.6 \times 10^{-3}$  s<sup>-1</sup> ( $\sim 5\%$  of the total ISOPO<sub>2</sub> sinks) and  $4.4 \times 10^{-3}$  s<sup>-1</sup> ( $\sim 7\%$  of the total MONOTERPO<sub>2</sub> sinks) in the tropical regions, respectively. The sensitivity analysis with 100% yield of individual product channels showed a further increment of HO<sub>2</sub> mixing ratios by up to 3.5% for (R11a), formation of ROOOH by up to 3 ppt for (R11d), formation of ROH by up to 800 ppt for (R11b) and formation of stabilized Criegee intermediates by up to  $12 \times 10^{-5}$  ppt for (R11c). The ROOOH generate secondary organic aerosol (SOA) of up to  $0.05$   $\mu\text{g m}^{-3}$  in the tropical region. This value is likely a lower limit as the study used yield of ROOOH,  $\phi_{\text{ROOOH}} = 0.11$  for all ROOOH, but with increasing size of the R, the formation of ROOOH could be the dominant product from (R11) and all these large sized ROOOH partition to form organic aerosol. Considering the yield = 1 for all large ROOOH, up to  $0.4$   $\mu\text{g per m}^3$  SOA is formed in tropical regions.

In previous work, we have made an intercomparison of the major chemical mechanisms employed in chemistry-transport (CTM) and earth system (ESM) models to describe the pre-industrial, present day and future air quality and greenhouse gas composition.<sup>58</sup> The composition data are essential to formulating global policies addressing global health impacts and global climate change. To our knowledge, few chemical mechanisms include any of the RO<sub>2</sub> + OH chemical reactions. A prerequisite for understanding the importance of the RO<sub>2</sub> + OH reactions is the inclusion of the RO<sub>2</sub> + OH reaction rate coefficients, together with their temperature dependences and reaction products, in the evaluated chemical kinetic data



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