Impacts of HO_x regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres.

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Abstract.

A global chemistry-climate model is used to assess the impact on atmospheric composition of the regeneration and recycling of HO_x in the photo-oxidation of isoprene. The impact is explored subject to present-day, pre-industrial and future climate/emission scenarios. Our calculations show that, in all cases, the inclusion of uni-molecular isomerisations of the isoprene hydroxy peroxy radicals leads to enhanced production of HO_x radicals and ozone. The global burden of ozone increases by 25-36 Tg (8-18%), depending on the climate/emissions scenario, whilst the changes in OH lead to decreases in the methane lifetime of between 11% in the futureand 35% in the pre-industrial. Critically the size of the change in methane lifetime depends on the VOC/NO_x emission

ratio. The results of the present-day calculations suggest a certain amount of parameter refinement is still needed to reconcile the updated chemistry with field observations (particularly for HO_2+RO_2). However, the updated chemistry could have far-reaching implications for: future-climate predictions; projections of future oxidising capacity; and our understanding of past changes in oxidising capacity.

1.0: Introduction.

Isoprene (2-methyl-1,3-butadiene) emissions comprise a major fraction of total biogenic volatile organic compound (BVOC) emissions. Field and modelling studies estimate that the natural emissions of isoprene have been fairly constant over the last decade or so, ~400-500 Tg C/yr [Müller et al., 2008]. Owing to the high reactivity of isoprene towards the hydroxyl radical (OH), model studies invariably implicate isoprene as a large sink of OH. However, the reactive products formed from the oxidation of isoprene by OH, the isoprene hydroxy-peroxy radicals (ISOPOHO2), can interact with oxides of nitrogen (NO_x = NO+NO_2) resulting in production of ozone in the troposphere—the main OH precursor.

Recent field studies in major isoprene emitting regions such as Amazonia [Lelieveld et al., 2008] and South East Asia [Hewitt et al., 2010] have found large discrepancies between modelled and measured HO_x concentrations. These discrepancies are not confined to the tropics, but coincide with regions impacted by isoprene emissions [Hofzumahaus et al., 2009; Tan et al., 2001]. The model-measurement disagreement is most pronounced where high isoprene concentrations (> 1 ppbv) coincide with low NO_x concentrations (< 1 ppbv). Several theoretical [Peeters et al., 2009; Peeters and Müller 2010; da Silva et al., 2010] and experimental [Paulot et al., 2009] studies have recently provided new insights into the oxidation mechanism of isoprene. No doubt, more studies will be required to unravel its intricacies. However, the work of Peeters et al. [2009] concerning unimolecular reactions of ISOPOHO2, has been shown in both box model [Archibald et al., 2010]

and global models [Archibald et al., 2010; Stavrakou et al., 2010] to improve the representation of low-NO_x isoprene chemistry.

We use the UKCA global chemistry-climate model (http://www.ukca.ac.uk) to explore the impact of including isomerisation reactions of ISOPOHO2 on the composition of the atmosphere in the present (2000), pre-industrial (*ca*. 1850) and future (2100). There exists a great deal of work in the literature about the importance of isoprene oxidation in global chemistry [e.g. Wang and Shallcross, 2000], and more recently, a great deal of debate towards the issues of reconciling problems with representing its chemistry in global models [Lelieveld et al., 2008; Archibald et al., 2010; Stavrakou et al., 2010]. There are likely to be modifications to the mechanism of isoprene oxidation as time progresses, but this work investigates the most important aspect that has been thus far poorly represented – the regeneration of HO_x radicals through isomerisation reactions of ISOPOHO2.

2.0: Method.

A number of experiments with the UKCA model, run at a horizontal resolution of 3.75º in longitude × 2.5º in latitude on 60 hybrid height levels that stretch from the surface to ~84 km, where carried out. The model set up is similar to that described in Telford et al. [2010], with a chemical mechanism comprising 60 chemical tracers and 132 photochemical reactions, including the oxidation of isoprene based on the Mainz Isoprene Mechanism [Pöschl et al., 2000]. The model's dynamical core is based on the Met Office's Unified Model version 6.1. In each experiment, the model is allowed to run freely with the climate forced by specified concentrations of long-lived greenhouse gases and ozone-depleting substances, in addition to prescribed sea surface temperatures and sea-ice coverage from the HadISST dataset [Rayner et al., 2003]. Stratospheric chemistry is not calculated explicitly. Instead, the concentrations of ozone and NO_y above 30 hPa are taken from the Cambridge 2D model [Law and Pyle, 1993] and are not changed between

79 experiments, so that the influence of the stratosphere on the troposphere remains constant. The
80 results are taken from three-year integrations following an 18 month 'spin-up' period.
81
82 Our modifications to the isoprene mechanism follows that applied in the global model STOCHEM,
83 in the study of Archibald et al. [2010] (their reactions R24-R26). However, the representation used
84 in this study differs somewhat from Archibald et al. [2010] as we omit the formation of the
85 (predicted) highly photolabile hydroperoxy-aldehyde (HPALD) and instead assume prompt
86 formation of OH from both isomerisations of the ISOPOHO2. The two reaction pathways are
87 represented by Eq. 1 and 2 (k_1 = 4.0×10^{-3} s^{-1}; k_2 = 8.0×10^{-2} s^{-1}; MACR=lumped C4 carbonyl;
88 MGLY=methyl glyoxal; HACET=hydroxyacetone). The product yields were determined by running
89 a series of box model experiments and optimising the product yields to give a reasonable match to
90 the results of Mechanism 4 of Archibald et al. [2010] for HO_x, ozone and CO. The values used for
91 k_1 and k_2 come from Archibald et al. [2010], derived for conditions appropriate for the tropics. Both
92 k_1 and k_2 are predicted to have significant temperature dependence (Peeters and Müller [2010]
93 predict variations of up to a factor of 3 for a 10 K change in temperature). However, owing to the
94 fact that most isoprene is oxidised in the tropics (near the surface) where there is small variation in
95 temperature, it is expected that this simplification should have only a relatively small impact on the
96 results.
97
98 ISOPOHO2 → OH + MACR + HCHO (Eq 1)
99 ISOPOHO2 → $1.0\times HO_2$ + 1.0×MGLY + 0.65×HACET + 0.6×OH (Eq 2)
100
101 Six experiments where carried out: a Base run (B) and a Modified run (M; including the
102 isomerisation reactions of ISOPOHO2) each subject to Present-Day (PD), Pre-Industrial (PI) and
103 Future (FC) climate/emissions scenarios (see Table 1 for a breakdown of the emissions), based on
104 the emissions of Stevenson et al. [2006], Lamarque et al. [2010] and Dentener et al. [2005]

105 respectively. The future emissions reflect the IPCC B2+CLE scenario. Note the relatively similar
106 total BVOC emissions, but much lower total NO_x emissions, in the pre-industrial, compared with
107 the present. In all cases the amount of CH_4 is prescribed (Table 1). In each period, we assessed the
108 impact of the updated isoprene scheme in terms of absolute differences (i.e. M-B) and percentage
109 differences (i.e. 100×((M–B)/B)). We assessed the changes in the troposphere only and define this
110 layer based on the lapse rate.
111
112 **3.0: Results.**
113
114 **3.1: Present day.**
115 In general our base present-day simulation (PD-B) generates results for ozone and CO that are
116 consistent with a wide range of observations and compare well with other global models (Fig 1)
117 [c.f. Stevenson et al., 2006; Shindell et al., 2006]. A comparison against ozone-sonde measurements
118 is shown in Fig 1a (PD-B indicated by red line and pink envelope). In general, and in line with the
119 majority of models [e.g. Shindell et al., 2006], the PD-B simulation tends to under-predict CO in the
120 Northern Hemisphere and slightly over predict CO in the Southern Hemisphere (red line in Fig 1b).
121 Including the ISOPOHO2 isomerisation reactions (PD-M, indicated by blue line and purple
122 envelope in Fig 1a) leads to an improvement in the comparison with ozone for almost all latitude
123 and pressure bands (the exception being Equator-30ºN, 750hPa). Likewise, there is improved
124 simulation of CO and the SH high bias is slightly reduced in the PD-M simulation (blue line in Fig
125 1b). The levels of OH and HO_2 are enhanced by as much as 410% and 225% respectively in certain
126 regions at the surface and up to 75% in the zonal mean (Fig 2). These enhancements are
127 approaching those needed to reproduce the high concentrations of OH and HO_2 measured in the
128 tropics [Lelieveld et al., 2008]. Note that the greatest increases in OH are mainly limited to surface
129 regions in the tropics, where there are high emissions of isoprene but low emissions of NO_x. Fig 2d
130 clearly shows that surface increases are propagated throughout the tropical free troposphere. These

131 increases in the free troposphere are driven by convection in the tropics lifting the products of
132 isoprene oxidation (such as MGLY in Eq 2) to higher altitudes where rapid photolysis allows
133 enhanced production of HO_2. In our parameterisation of the products of the ISOPOHO2
134 isomerisation's MGLY is included as a major product. Our PD-M simulation tends to predict
135 concentrations of MGLY which are comparable but higher (around a factor of two) than those
136 reported by Fu et al. [2008]. The exact products following ISOPOHO2 isomerisation's are in need
137 of experimental verification. However, our representation of them as small oxidised compounds
138 known to be associated with isoprene oxidation should, to first order, have only a small effect on the
139 results.
140
141 In Fig 1c we compare modelled and measured OH and HO_2+RO_2 made during the OP3 campaign in
142 Borneo [Hewitt et al., 2010]. The PD-M simulation (blue line) clearly improves the comparison
143 between modelled and measured OH. Reducing the rate of the ISOPOHO2 isomerisation's by a
144 factor of two (green lines) leads to a very small decrease in the OH enhancement compared with the
145 PD-M run. However, it is apparent from analysis of the HO_2+RO_2 data that some form of parameter
146 refinement is needed as the PD-M mechanism over simulates the amount of HO_2+RO_2 by more than
147 a factor of two. We note that this is not unique to our implementation of the Peeters' mechanism;
148 both Stavrakou et al. [2010] and Whalley et al. [2011 in prep] also present results that show an over-
149 simulation of HO_2 relative to OH. Globally, the amount of OH in the troposphere increases
150 significantly (Table 2) leading to a decrease in the lifetime of methane, of around 14%. The amount
151 of ozone also increases by some 25 Tg (8%) globally. This is driven by a reduction in the flux of
152 ozonolysis and by an increase in the flux through the reaction between HO_2 and NO. The level of
153 enhancement in HO_x in the present study is much greater than that reported by Archibald et al.
154 [2010] where at most they calculated increases of ~50%. This can be attributed to an overestimation
155 in that study of NO_x in isoprene rich areas, with the present results being more in line with the work
156 of Peeters and Müller [2010] and Stavrakou et al. [2010].

157

158

159 **3.2: Pre-industrial.**

160 As in previous studies [Mickley et al., 2001; Lamarque et al., 2005], our base pre-industrial
161 calculations (PI-B) cannot reproduce the very low concentrations of surface ozone measured at the
162 turn of the 20th century using the Schonbein method [Pavelin et al., 1999]. Mickley et al. [2001]
163 suggested this could be the result of an overestimation of NO_x emissions at that time. They also
164 postulated that increased emissions of reactive BVOCs could contribute, although Lamarque et al.
165 [2005] have subsequently argued that this would be inconsistent with our best estimates of PI
166 emissions. More recently, Pavalla et al. [2010] have reported that the inclusion of tropospheric
167 halogen chemistry can help to resolve this.

168

169 Like Mickley et al. [2001], we find that the combination of low levels of NO_x and the propensity for
170 isoprene to react with OH leads to near titration of OH in much of the continental boundary layer in
171 the tropics and mid-latitudes in our PI-B experiment. When we include the updates to the chemistry
172 (PI-M), as with the present-day, we calculate significant enhancements in OH and HO_2, but in the
173 pre-industrial this is to a much greater extent owing to the lower levels of NO_x. We calculate
174 enhancements in OH approaching 1500% in some regions at the surface, and 170% in the zonal
175 mean (in the tropics near the surface, see Fig 2); HO_2 is enhanced by as much as 300% at the
176 surface and 75% in the zonal mean. Enhanced destruction of CO in the boundary layer leads to
177 lower levels of CO, and higher levels of OH, throughout much of the troposphere. Globally, the
178 increase in OH leads to a 35% reduction in the lifetime of methane—a very substantial
179 decrease—whilst we calculate an increase in global ozone burden of 36 Tg (18%).

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181

182 **3.3: Future.**

183 We explored a reasonably optimistic future-emissions scenario (IPCC B2+CLE), in which NO_x
184 emissions decrease but VOC emissions increase. We note that the increased emissions of isoprene
185 do not reflect the important role that CO_2 inhibition may play in a CO_2-warmed future [Young et al.,
186 2009]. The results of the base simulation (FC-B) are generally similar to the PD-B simulation,
187 although we simulate an increase in ozone of ~32 Tg. Similarly, on updating the chemistry (FC-M)
188 we calculate enhancements in OH and HO_2 of as much as 550% and 200% respectively at the
189 surface and greater than 75% for OH in the tropics near the surface as a zonal mean (see Fig 2). The
190 increased HO_x then leads to further increases in ozone burden (32 Tg or ~9%) and a significant
191 reduction in the lifetime of methane of ~11%.
192
193 **4.0: Discussion and conclusions.**
194 Implementing updated (low NO_x) chemistry for isoprene has led to large increases in modelled HO_x
195 concentrations. These increases are largest within the boundary layer in regions where NO_x
196 concentrations are low and isoprene concentrations are high. These areas are predominantly found
197 in the tropics. Deep convection in these areas lifts the products of isoprene oxidation into the free
198 troposphere and promotes ozone production (mainly through an increase in the reaction between
199 HO_2 and NO). Ultimately, the modified isoprene chemistry is sensitive to the chemical environment
200 which can be characterised on a global scale by the ratio of VOC/NO_x emissions. Characterising the
201 global effects of this modified chemistry by comparing relative changes in the methane lifetime
202 shows that there is a tailing off in the importance of the effect, from the pre-industrial to a warmer,
203 "cleaner" future. However, the importance of understanding the evolution in atmospheric
204 composition should not be underestimated. The changes in ozone burden (Table 2) (and to a lesser
205 extent methane lifetime) have bearings on future-climate predictions, owing to the radiative-forcing
206 properties of these greenhouse gases, whilst the changes in methane lifetime have consequences for
207 projections of future oxidising capacity, and our understanding of past changes in oxidising
208 capacity—an area we intend to explore further. The Peeters mechanism [Peeters et al., 2009] is

unlikely to be the last word on the subject but its contribution to our understanding of the chemistry surrounding isoprene oxidation at low-NO_x concentrations has potentially far-reaching implications. These warrant further study and validation via model-measurement comparison and crucially targeted laboratory experiments aimed at simulating the conditions encountered in the tropical boundary layer.

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Captions:

312 Table 1. Prescribed methane levels (mixing ratios in ppmv) and emissions for the three sets of
313 simulations. All emissions are given as global yearly averages in Tg of species emitted. See text for
314 sources of emissions.
315
316 Table 2. Tropospheric burdens of O_3, OH and CO for each model run. Troposphere defined using
317 lapse rate tropopause (see Figure 2).
318
319 Figure 1. Comparison of PD results with observations. Panel (a) comparison with ozone-sonde data
320 (data from Logan [1999] and Thompson et al. [2003a, 2003b]). Panel (b) comparison with surface
321 CO measurements (data from the NOAA GMD network [Novelli et al., 1998]). Panel (c)
322 comparison with surface observations made during the OP3 campaign in Borneo. OH data are
323 measured using Leeds FAGE instrument [Whalley et al., 2010], RO_2+HO_2 are measured using
324 Leicester PERCA instrument [Fleming et al., 2006]. In all cases observations are given by black
325 lines and symbols, with the PD-B data given by red lines and dots and the PD-M data by blue lines
326 and dots. Sensitivity simulations are shown in Panel (c) for reducing the rates of k_1+k_2 by half
327 (green lines).
328
329 Figure 2. Multiannual mean surface (less than 600m) and zonal changes in OH, CO and O_3 between
330 Modified run and Base run for three climate/emission scenarios. Changes in O_3 and CO are
331 expressed as absolute changes (Mod-Base), changes in OH presented as percentage changes ((Mod-
332 Base)/Base)×100. Surface changes shown for PD conditions only. Zonal plots have the respective
333 height of the tropopause superimposed (thick black dashed line) for each scenario (Note figures are
334 clipped in height to focus attention on the effects in the troposphere.).
335
336 **Tables and Figures:**
337 Table 1.

	NO_2	CO	HCHO	C_2H_6	C_3H_8	Acetone	CH_3CHO	C_5H_8	CH_4
PI (1860)	34.3	434.7	4.1	10.2	3.7	43.8	6.7	573	0.790
PD (2000)	147	1078.1	6.3	51.1	48.5	65.3	24.2	467.1	1.655
FC (2100)	122.9	1039.5	5.7	45.8	42.3	63.1	22.4	545.3	2.973

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345 Table 2.

Run	Ozone Burden (Tg)	OH Burden (Tg)	CO Burden (Tg)
PI-B	194	7.74×10^{-5}	347
PI-M	230	1.16×10^{-4}	280
PD-B	323	1.15×10^{-4}	432
PD-M	348	1.34×10^{-4}	404
FC-B	347	1.04×10^{-4}	567
FC-M	380	1.21×10^{-4}	543

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