Supplementary Information: Improvements to the representation of BVOC chemistry-climate interactions in UKCA (vn11.5) with the CRI-Strat 2 mechanism: Incorporation and Evaluation

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- 28 Section S129

30 1.1 Updates to CS to produce CS2

- 32 CRI-STRAT (CS) reactions are shown in black, CRI-STRAT 2 (CS2) reactions in red. Pairings show a direct swap 33 while struck-through black reactions indicate CS reactions which were removed with no direct replacement. Red 34 reactions without a black partner reaction are new reactions to the CS2. For termolecular reactions, complex rate 35 constants are used and in these cases the low pressure limit (k_0), high pressure limit (k_1) and F_c value are specified.
- 36

- 37 Termolecular Reactions
- **38** O(3P) + NO = NO2: $k_0 = 9 \times 10^{-32} [M] (T/300)^{-1.5}, k_1 = 3 \times 10^{-11} F_c = 0.6$
- **39** O(3P) + NO = NO2: $k_0 = 1 \times 10^{-31} [M] (T/300)^{-1.6}, k_1 = 5 \times 10^{-11} (T/300)^{-0.3} F_c = 0.85$ **40**
- **41** O(3P) + NO2 = NO3: $k_0 = 9 \times 10^{-32} [M] (T/300)^{-2}, k_1 = 2.2 \times 10^{-11} F_c = 0.6$
- 42 O(3P) + NO2 = NO3: $k_0 = 1.30 \times 10^{-31} [M] (T/300)^{-1.5}, k_1 = 2.30 \times 10^{-11} (T/300)^{0.24} F_c = 0.6$ 43
- 44 HO2 + NO2 = HO2NO2: $k_0 = 1.80 \times 10^{-31} [M] (T/300)^{-3.2}, k_1 = 4.70 \times 10^{-12} F_c = 0.6$
- **45** HO2 + NO2 = HO2NO2: $k_0 = 1.40 \times 10^{-31} [M] (T/300)^{-3.1}, k_1 = 4.00 \times 10^{-12} F_c = 0.4$

46	
47	OH + NO = HONO: $k_0 = 7.40 \times 10^{-31} [M] (T/300)^{-2.4}, k_1 = 3.30 \times 10^{-11} (T/300)^{-0.3} F_c = e^{-T/1420}$
48	OH + NO = HONO: $k_0 = 7.40 \times 10^{-31} [M] (T/300)^{-2.4}, k_1 = 3.30 \times 10^{-11} (T/300)^{-0.3} F_c = 0.81$
49	
50	OH + NO2 = HONO2: $k_0 = 2.60 \times 10^{-30} [M] (T/300)^{-3.2}, k_1 = 2.40 \times 10^{-11} (T/300)^{-1.3} F_c = 0.6$
51 52	OH + NO2 = HONO2: $k_0 = 3.20 \times 10^{-30} [M] (T/300)^{-4.5}, k_1 = 3.00 \times 10^{-11} F_c = 0.41$
53	MeCO3 + NO2 = PAN: $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$
54 55	MeCO3 + NO2 = PAN: $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$
56	EtCO3 + NO2 = PPAN: $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$
57 58	EtCO3 + NO2 = PPAN: $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$
59	NO2 + NO3 = N2O5: $k_0 = 2.20 \times 10^{-30} [M] (T/300)^{-3.90}, k_1 = 1.50 \times 10^{-12} (T/300)^{-0.7} F_c = 0.60$
60	NO2 + NO3 = N2O5 : $k_0 = 3.60 \times 10^{-30} [M] (T/300)^{-4.10}$, $k_1 = 1.90 \times 10^{-12} (T/300)^{-0.2} F_c = 0.35$
61	
62	HOCH2CO3 + NO2 = PHAN : $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$
63 64	HOCH2CO3 + NO2 = PHAN : $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$
65	RTN26O2 + NO2 = RTN26PAN : $k_0 = 6.14 \times 10^{-29} [M] (T/300)^{-6.87}, k_1 = 7.94 \times 10^{-12} (T/300)^{-1.0} F_c = 0.60$
66 67	RTN26O2 + NO2 = RTN26PAN : $k_0 = 2.368 \times 10^{-28} [M] (T/300)^{-6.50}, k_1 = 8.123 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$
68	$\frac{\text{RU12O2} + \text{NO2} - \text{RU12PAN}}{\text{RU12O2} + \text{NO2} - \text{RU12PAN}} : k_0 = 5.19 \times 10^{-30} [M] (T/300)^{-6.50}, k_1 = 6.71 \times 10^{-13} (T/300)^{-1.00} F_c = 0.60$
69	$\frac{\text{RU12PAN} - \text{RU12O2} + \text{NO2}}{100000000000000000000000000000000000$
70	
71 72	RU12O2 = DHCARB9 + CO + OH : $k = 2.40 \times 10^5 e^{-5300/T}$
73 74	MACO3 + NO2 = MPAN : $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.60$
75	MPAN = RU1002 + NO2 : $k_0 = 1.105 \times 10^{-5} [M] e^{-10100/T}$, $k_1 = 1.90 \times 10^{17} e^{-14100/T} F_c = 0.30$
76 77	MPAN = MACO3 + NO2 : $k = 1.60 \times 10^{16} e^{-13500/T}$
78	RU14O2 = 0.5DHPR12O2 + 0.5 HPUCARB12 + 0.5 HO2 : $k = 2.76 \times 10^7 e^{-6597/T} *$
79	RU14O2 = UCARB10 + OH + CO: $k = 1.24 \times 10^{11} e^{-9570/T}$
80	DHPR12O2 = DHPCARB9 + CO + OH: $k = 3.0 \times 10^7 e^{-5300/T}$
81 82	RU10AO2 = CARB7 + CO + OH: $k = 3.0 \times 10^7 e^{-5300/T}$
83 84	*This reaction, along with 4 bimolecular reactions, allows the $k_{bulk1,6H}$ rate constant to be represented in the framework of UKCA.
85 86	Photolysis Reactions
87	CARB3 + PHOTON = CO + CO + HO2 + HO2 : 9.46*jhchoa
88	CARB3 + PHOTON = CO + CO + HO2 + HO2 : Glyxla from Prather et al (2013)
89 00	CARB3 + PHOTON = CO + CO + H2 : Glyxlb from Prather et al (2013)
90 91	CARBS + PHOTON = HCHO + HO2 : Glyxic from Pratner et al (2013)
92	$\frac{TNCARB12 + PHOTON - RN9O2 + HOCH2CO3 + 5.47e}{4*ino2}$
93 94	$\frac{1}{1000} = \frac{1}{1000} = 1$
95	UCARB12 + PHOTON = MeCO3 + HOCH2CHO + CO + HO2 : jhchoa
96	UCARB12 + PHOTON = MeCO3 + HOCH2CHO + CO + HO2 : 0.25*jhchoa
97	UCARB12 + PHOTON = RU12O2 + HO2 : 0.5*jmacr
98	UCARB12 + PHOTON = CARB7 + CO + CO + HO2 + HO2 : 0.25*jmacr
99 100	NUCADD12 + DUOTON = NOA + CO + CO + UO2 + image
101	$\frac{1}{1000} = \frac{1000}{100} = 1000$
102	Accinente a filoration and filor and filor and filor
103	NRU12OOH + PHOTON = NOA + CO + HO2 + OH: jmhp

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NRU12OOH + PHOTON = NOA + CO + HO2 + OH: jmhp
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104 NRU12OOH + PHOTON = NOA + CARB3 + HO2 + OH: jmhp 105 106 RU14NO3 + PHOTON = UCARB10 + HCHO + HO2 + NO2 : jiprn 107 RU12NO3 + PHOTON = CARB6 + HOCH2CHO + HO2 + NO2 : 7.583e-3*jno2 108 RU10NO3 + PHOTON = MeCO3 + HOCH2CHO + NO2 : 1.213e-3*jno2 109 110 HPUCARB12 + PHOTON = HUCARB9 + CO + OH + OH : 91.65*jmacr 111 HPUCARB12 + PHOTON = CARB7 + CO + CO + HO2 + OH : 91.65*imacr112 HUCARB9 + PHOTON = CARB6 + CO + HO2 + OH : 91.65*jmacr 113 114 DHPR12OOH + PHOTON = DHPCARB9 + CO + OH + HO2 : jetcho 115 DHPR12OOH + PHOTON = CARB3 + RN8OOH + OH + OH : 3*jmhp 116 117 DHCARB9 + PHOTON = CARB7 + CO + HO2 + HO2 : jetcho 118 119 NUCARB12 + PHOTON = CARB7 + CO + CO + HO2 + NO2 : 6.066e-3*jno2 120 121 122 123 124 **Bimolecular Reactions** A significant number of the RO₂ + NO and RO₂ + NO₃ reactions changed only in their rate constants (rate constant changes shown below) and these changes are not listed here. Where the reactions changed in the branching ratio and/or products, the reactions are shown. CS: $k_{APNO} = 8.1 \times 10^{-12} e^{290/T}$ 125 126 CRI v2.2 $k_{APNO} = 7.5 \times 10^{-12} e^{290/T}$ 127 128 CS: $k_{RO2+NO} = 2.4 \times 10^{-12} e^{360/T}$ 129 CRI v2.2 $k_{R02+N0} = 2.7 \times 10^{-12} e^{360/T}$ 130 131 CS: $k_{R02+N0_3} = 2.5 \times 10^{-12}$ 132 CRI v2.2 $k_{R02+N0_3} = 2.3 \times 10^{-12}$ 133 134 $O(1D) + H2O = OH + OH : k = 2.20 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 135 $O(1D) + H2O = OH + OH : k = 2.14 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 136 137 $O(1D) + N2 = OH + OH : k = 1.80 \times 10^{-10} e^{110/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 138 $O(1D) + N2 = OH + OH : k = 2.00 \times 10^{-11} e^{130/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 139 140 O(1D) + O2 = OH + OH: $k = 3.20 \times 10^{-11} e^{70/T}$ cm³ molecules⁻¹ s⁻¹ 141 $O(1D) + O2 = OH + OH : k = 3.20 \times 10^{-11} e^{67/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ 142 143 144 $HO2 + NO = OH + NO2 : k = 3.60 \times 10^{-12} e^{270/T}$ 145 HO2 + NO = OH + NO2 : $k = 3.45 \times 10^{-12} e^{270/T}$ 146 147 OH + HO2NO2 = H2O + NO2 + O2 : $k = 1.90 \times 10^{-12} e^{270/T}$ 148 OH + HO2NO2 = H2O + NO2 + O2 : $k = 3.20 \times 10^{-13} e^{690/T}$ 149 150 OH + PAN = HCHO + CO + NO2 : $k = 9.50 \times 10^{-13} e^{-650/T}$ 151 $OH + PAN = HCHO + CO + NO2 : k = 3.40 \times 10^{-14}$ 152 153 $OH + MPAN = CARB7 + CO + NO2 : k = 3.60 \times 10^{-12}$ 154 $OH + MPAN = CARB7 + CO + NO2 : k = 6.38 \times 10^{-12}$ 155 156 OH + MeONO2 = HCHO + NO2 + H2O: $k = 1.00 \times 10^{-14} e^{-1060/T}$ 157 OH + MeONO2 = HCHO + NO2 + H2O: $k = 4.00 \times 10^{-13} e^{-845/T}$ 158 159 MeOO + NO = HCHO + NO2 + HO2: $k = 3.00 \times 10^{-12} e^{-280/T}$ 160 MeOO + NO = HCHO + NO2 + HO2: $k = 2.298 \times 10^{-12} e^{-360/T}$

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161
162
          MeOO + NO = MeONO2 : k = 3.00 \times 10^{-15} e^{-280/T}
163
          MeOO + NO = MeONO2 : k = 2.30 \times 10^{-15} e^{-360/T}
164
165
          MeOO + NO = HO2 + HCHO + NO2 : k = 1.00 \times 10^{-12}
166
          MeOO + NO3 = HO2 + HCHO + NO2 : k = 1.20 \times 10^{-12}
167
168
          NO3 + C5H8 = NRU14O2 : k = 3.0 \times 10^{-12} e^{-466/T}
169
          NO3 + C5H8 = NRU14O2 : k = 3.15 \times 10^{-12} e^{-450/T}
170
171
          O3 + C5H8 = UCARB10 + CO + HO2 + OH : k = 2.12 \times 10^{-15} e^{-1913/T}
          O3 + C5H8 = UCARB10 + HCOOH : k = 5.74 \times 10^{-15} e^{-1913/T}
172
          O3 + C5H8 = UCARB10 + CO + HO2 + OH : k = 1.288 \times 10^{-15} e^{-1995/T}
173
174
          O3 + C5H8 = HCHO + MeOO + CO + HO2 : k = 9.79 \times 10^{-16} e^{-1995/T}
175
          O3 + C5H8 = UCARB10 + HCOOH : k = 1.80 \times 10^{-15} e^{-1995/T}
176
          O3 + C5H8 = UCARB10 + HCHO + H2O2 : k = 3.97 \times 10^{-15} e^{-1995/T}
177
          O3 + C5H8 = MeCO3 + HCHO + CO + OH : k = 1.29 \times 10^{-15} e^{-1995/T}
178
          O3 + C5H8 = UCARB10 + CO : k = 9.785 \times 10^{-16} e^{-1995/T}
179
          OH + C5H8 = RU14O2 : k = 2.54 \times 10^{-12} e^{410/T}
180
181
          OH + C5H8 = RU14O2 : k = 2.70 \times 10^{-12} e^{390/T}
182
183
          OH + UCARB10 = RU10O2 : k = 2.50 \times 10^{-11}
184
          OH + UCARB10 = RU10O2 : k = 3.84 \times 10^{-12} e^{533/T}
185
186
          NO3 + UCARB10 = RU10O2 + HONO2 : k = 1.44 \times 10^{-12} e^{-1862/T}
187
          NO3 + UCARB10 = RU10O2 + HONO2: k = 5.98 \times 10^{-13} e^{-1862/T}
188
189
          O3 + UCARB10 = HCHO + MeCO3 + CO + OH : k = 1.68 \times 10^{-18}
190
          O3 + UCARB10 = HCHO + MeCO3 + CO + OH : k = 3.84 \times 10^{-16} e^{-1710/T}
191
192
          O3 + UCARB10 = HCHO + CARB6 + H2O2 : k = 1.17 \times 10^{-18}
193
          O3 + UCARB10 = HCHO + CARB6 : k = 8.16 \times 10^{-16} e^{-1710/T}
194
195
          OH + UCARB12 = RU10O2 : k = 4.52 \times 10^{-11}
196
          OH + UCARB12 = RU10O2 : k = 6.42 \times 10^{-11}
197
198
          NO3 + UCARB12 = RU10O2 : k = 4.52 \times 10^{-11}
199
          NO3 + UCARB12 = RU10O2 : k = 6.42 \times 10^{-11}
200
201
          O3 + UCARB12 = HOCH2CHO + MeCO3 + CO + OH : k = 2.14 \times 10^{-17}
202
          O3 + UCARB12 = HOCH2CHO + MeCO3 + CARB3 + OH : k = 6.00 \times 10^{-18}
203
          O3 + UCARB12 = HOCH2CHO + CARB6 + H2O2 : k = 2.64 \times 10^{-18}
204
205
          O3 + UCARB12 = CARB6 + CO + OH + HO2 : k = 1.20 \times 10^{-17}
206
207
          OH + RU14OOH = UCARB12 + OH: k = 7.51 \times 10^{-11}
208
          OH + RU14OOH = 0.09UCARB12 + 0.94OH + 0.85IEPOX + 0.06RU14O2: k = 7.14 \times 10^{-11}
209
210
          OH + RU12OOH = RU12O2: k = 3.00 \times 10^{-11}
211
          OH + RU12OOH = RU10OOH + CO + HO2: k = 3.50 \times 10^{-11}
212
213
          OH + RU10OOH = RU10O2: k = 3.00 \times 10^{-11}
214
          OH + RU10OOH = CARB7 + CO + OH: k = 3.84 \times 10^{-11}
215
216
          MPAN + OH = HMML + NO3: k = 2.262 \times 10^{-11}
217
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218
          RU10O2 + NO3 = CARB7 + HCHO + HO2 + NO2 : k = 5.00 \times 10^{-13}
219
          RU10AO2 + NO3 = CARB7 + HCHO + HO2 + NO2 : k = 2.30 \times 10^{-12}
220
221
          RU10O2 + RO2 = CARB7 + HCHO + HO2 : k = 4.00 \times 10^{-13}
222
          RU10AO2 + RO2 = CARB7 + CO + HO2 : k = 3.60 \times 10^{-13}
223
224
225
          RU10AO2 + NO = CARB7 + CO + HO2 : k = 2.665 \times 10^{-12} e^{360/T}
226
227
          RU10AO2 + HO2 = RU10OOH + CO + HO2 : k = 1.819 \times 10^{-13} e^{1300/T}
228
229
          OH + CARB3 = CO + OH : k = 6.2 \times 10^{-13} e^{340/T}
230
231
          DHPR12O2 + NO = CARB3 + RN8OOH + OH + NO2 : k = 2.70 \times 10^{-12} e^{360/T};
232
          DHPR12O2 + NO3 = CARB3 + RN8OOH + OH + NO2 : k = 2.30 \times 10^{-12};
233
          DHPR12O2 + HO2 = DHPR12OOH : k = 2.91 \times 10^{-13} e^{1300/T} * 0.706;
234
          DHPR12O2 + RO2 = CARB3 + RN8OOH + OH : k = 7.60 \times 10^{-13};
235
236
          OH + HUCARB9 = CARB6 + CO + HO2 : k = 5.78 \times 10^{-11};
237
238
          OH + DHCARB9 = CARB6 + HO2 : k = 3.42 \times 10^{-11};
239
240
          OH + DHPCARB9 = RN8OOH + CO + OH : k = 3.64 \times 10^{-11}
241
242
          RU12O2 + NO = CARB7 + HOCH2CO3 + NO2 : k = 4.59 \times 10^{-13} e^{360/T}
243
          RU12O2 + NO3 = CARB7 + HOCH2CO3 + NO2 : k = 4.05 \times 10^{-13}
244
245
          OH + IEPOX = RU12O2 : k = 1.16 \times 10^{-11}
246
247
          OH + HMML = CARB6 + OH : k = 4.33 \times 10^{-12} * 0.7;
248
          OH + HMML = HCOOH + CH3CO3 : k = 4.33 \times 10^{-12} * 0.3;
249
          OH + DHPR12OOH = DHPCARB9 + CO + OH : k = 5.64 \times 10^{-11};
250
          OH + RU12NO3 = CARB7 + CARB3 + NO2 : k = 2.50 \times 10^{-12};
251
          OH + RU10NO3 = CARB7 + CO + NO2 : k = 5.26 \times 10^{-13};
252
253
          RU10AO2 + NO = RU10NO3 : k = 2.70 \times 10^{-12} e^{360/T} * 0.013 :
254
          RU10AO2 + NO = CARB7 + CO + HO2 + NO2 : k = 2.70 \times 10^{-12} e^{360/T} * 0.987;
255
          RU10AO2 + NO3 = CARB7 + CO + HO2 + NO2 : k = 2.30 \times 10^{-12};
256
          RU10AO2 + HO2 = RU10OOH : k = 2.91 \times 10^{-13} e^{1300/T} * 0.625;
257
          RU10AO2 + RO2= CARB7 + CO + HO2 : k = 3.60 \times 10^{-13}
258
259
          MACO3 + NO = CH3O2 + CO + HCHO + HO2 + NO2 : k = 7.50 \times 10^{-12} e^{290/T} * 0.65;
260
          MACO3 + NO = CH3CO3 + HCHO + HO2 + NO2 : k = 7.50 \times 10^{-12} e^{290/T} * 0.35;
261
          MACO3 + NO3 = CH3O2 + CO + HCHO + HO2 + NO2 : k = 2.30 \times 10^{-12} \times 1.74 \times 0.65;
262
          MACO3 + NO3 = CH3CO3 + HCHO + HO2 + NO2 : k = 2.30 \times 10^{-12} * 1.74 * 0.35;
263
          MACO3 + HO2 = RU10OOH : k = 5.20 \times 10^{-13} e^{980/T} * 0.56;
264
          MACO3 + HO2 = CH3O2 + CO + HCHO + OH : k = 5.20 \times 10^{-13} e^{980/T} *0.44;
265
266
          OH + HPUCARB12 = HUCARB9 + CO + OH : k = 5.20 \times 10^{-11};
267
          O3 + HPUCARB12 = CARB3 + CARB6 + OH + OH : k = 2.4 \times 10^{-17};
268
          NO3 + HPUCARB12 = HUCARB9 + CO + OH + HNO3 : k = 1.44 \times 10^{-12} e^{-1862/T} * 4.25;
269
270
          NRU12O2 + NO = NOA + CARB3 + HO2 + NO2 : k = 1.35 \times 10^{-12} e^{360/T}
271
          NRU12O2 + NO3 = NO3 + CARB3 + HO2 + NO2 : k = 1.15 \times 10^{-12};
272
          NRU12O2 + RO2 = NOA + CARB3 + HO2 + NO2 : k = 4.80 \times 10^{-13};
273
          RU12O2 + RO2 = CARB7 + HOCH2CO3 : k = 7.392 \times 10^{-14}
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274
          HOCH2CO3 + HO2 = HCHO + HO2 + OH : k = 2.288 \times 10^{-13} e^{980/T}
275
276
          RU14NO3 + OH = RU12NO3 + HO2 : k = 5.40 \times 10^{-12}
277
          RU14NO3 + OH = RU10NO3 + HCHO + HO2 : k = 1.44 \times 10^{-11}
278
279
280
          *RU14O2 + NO = 0.5HPUCARB12 + 0.5HO2 + 0.5DHPR12O2 + NO : k = 1.399 \times 10^{-15} e^{1668/T}
281
          *RU14O2 + NO3 = 0.5HPUCARB12 + 0.5HO2 + 0.5DHPR12O2 + NO3: k = 1.191 \times 10^{-15} e^{1308/T}
282
          *RU14O2 + HO2 = 0.5HPUCARB12 + 0.5HO2 + 0.5DHPR12O2 + HO2 : k = 1.064 \times 10^{-15} e^{2608/T}
283
          *RU14O2 + RO2 = 0.5HPUCARB12 + 0.5HO2 + 0.5DHPR12O2 + RO2 : k = 6.527 \times 10^{-16} e^{1308/T}
284
285
          *These reactions, when combined with the unimolecular reaction RU14O2 = 0.5HPUCARB12 + 0.5HO2 + 0.5DHPR12O2, represents the k_{bulkl, 6H}
286
          rate constant in the framework of UKCA.
          EtOO + NO = MeCHO + HO2 + NO2: k = 2.58 \times 10^{-12} e^{365/T}
287
288
          EtOO + NO = RU10NO3 + HCHO + HO2 : k = 2.53 \times 10^{-12} e^{380/T}
289
          EtCO3 + HO2 = EtCO3H : k = 4.40 \times 10^{-13} e^{980/T}
290
291
          EtCO3 + HO2 = EtCO3H + HCHO + HO2 : k = 4.30 \times 10^{-13} e^{1040/T}
292
293
          EtOO + HO2 = EtOOH : k = 7.50 \times 10^{-13} e^{700/T}
294
          EtOO + HO2 = EtOOH : k = 4.30 \times 10^{-13} e^{870/T}
295
296
          MeCO3 + HO2 = MeCO3H : k = 4.31 \times 10^{-13} e^{1040/T}
297
          MeCO3 + HO2 = MeCO3H : k = 2.91 \times 10^{-13} e^{980/T}
298
299
          MeCO3 + HO2 = MeOO + OH : k = 2.29 \times 10^{-13} e^{980/T}
300
301
          NO + HO2 = NO2 + OH : k = 3.60 \times 10^{-12} e^{270/T}
302
          NO + HO2 = NO2 + OH : k = 3.45 \times 10^{-12} e^{270/T}
303
304
          MeOO + NO = HCHO + HO2 + NO2 : k = 3.00 \times 10^{-12} e^{280/T}
305
          MeOO + NO = HCHO + HO2 + NO2 : k = 2.298 \times 10^{-13} e^{360/T}
306
307
          MeOO + NO = MeONO2 : k = 3.00 \times 10^{-15} e^{280/T}
308
          MeOO + NO = MeONO2 : k = 2.30 \times 10^{-15} e^{360/T}
309
310
          MeOO + NO3 = HO2 + HCHO + NO2 : k = 1.00 \times 10^{-12}
311
          MeOO + NO3 = HO2 + HCHO + NO2 : k = 1.20 \times 10^{-12}
312
313
          HCHO + NO3 = HONO2 + HO2 + CO : k = 5.80 \times 10^{-16}
314
          HCHO + NO3 = HONO2 + HO2 + CO : k = 5.50 \times 10^{-16}
315
316
          MeCHO + NO3 = HONO2 + HO2 + CO : k = 1.44 \times 10^{-12} e^{-1862/T}
317
          MeCHO + NO3 = HONO2 + HO2 + CO : k = 1.40 \times 10^{-12} e^{-1860/T}
318
319
          EtCHO + OH = H2O + EtCO3 : k = 1.96 \times 10^{-11}
320
          EtCHO + OH = H2O + EtCO3 : k = 4.90 \times 10^{-12}
321
322
          MeCHO + OH = H2O + MeCO3 : k = 5.55 \times 10^{-12} e^{311/T}
323
          MeCHO + OH = H2O + MeCO3 : k = 4.70 \times 10^{-12} e^{345/T}
324
325
          MeOOH + OH = H2O + HCHO + OH : k = 1.02 \times 10^{-12} e^{190/T}
326
          MeOOH + OH = H2O + HCHO + OH : k = 2.12 \times 10^{-12} e^{190/T}
327
328
          O3 + C2H4 = H2O + HCHO + OH : k = 1.19 \times 10^{-15} e^{-2580/T}
329
          O3 + C2H4 = H2O + HCHO + OH : k = 1.18 \times 10^{-15} e^{-2850/T}
330
          O3 + C2H4 = HCHO + HCOOH : k = 7.95 \times 10^{-15} e^{-2580/T}
```

O3 + C2H4 = HCHO + HCOOH : $k = 7.91 \times 10^{-15} e^{-2850/T}$ NO3 + C2H4 = NRN602 : $k = 2.10 \times 10^{-16}$ NO3 + C2H4 = NRN9O2: $k = 3.30 \times 10^{-12} e^{-2880/T}$ OH + TOLUENE = AROH17 + HO2 : $k = 3.26 \times 10^{-13} e^{338/T}$ OH + TOLUENE = AROH17 + HO2 : $k = 3.24 \times 10^{-12} e^{340/T}$ OH + TOLUENE = RA16O2 : $k = 1.48 \times 10^{-12} e^{338/T}$ OH + TOLUENE = RA16O2 : $k = 1.48 \times 10^{-12} e^{340/T}$ NO3 + APINENE = NRTN28O2 : $k = 1.19 \times 10^{-12} e^{490/T}$ NO3 + APINENE = NRTN28O2 : $k = 1.20 \times 10^{-12} e^{490/T}$ O3 + APINENE = OH + Me2CO + RN18AO2 : $k = 8.08 \times 10^{-16} e^{-732/T}$ O3 + APINENE = OH + Me2CO + RN18AO2 : $k = 6.44 \times 10^{-16} e^{-644/T}$ O3 + APINENE = TNCARB26 + H2O2 : $k = 7.57 \times 10^{-17} e^{-732/T}$ O3 + APINENE = TNCARB26 + H2O2 : $k = 1.41 \times 10^{-16} e^{-644/T}$ O3 + APINENE = RCOOH25 : $k = 1.26 \times 10^{-16} e^{-732/T}$ O3 + APINENE = RCOOH25 : $k = 2.01 \times 10^{-17} e^{-644/T}$ O3 + BPINENE = RTX24O2 + OH : $k = 5.25 \times 10^{-18}$ O3 + BPINENE = RTX24O2 + OH : $k = 4.73 \times 10^{-16} e^{-1270/T}$ O3 + BPINENE = HCHO + TXCARB24 + H2O2 : $k = 3.00 \times 10^{-18}$ O3 + BPINENE = HCHO + TXCARB24 + H2O2 : $k = 2.70 \times 10^{-16} e^{-1270/T}$ O3 + BPINENE = HCHO + TXCARB22 : $k = 3.75 \times 10^{-18}$ O3 + BPINENE = HCHO + TXCARB22 : $k = 3.38 \times 10^{-16} e^{-1270/T}$ $O3 + BPINENE = CO + TXCARB24 : k = 3.00 \times 10^{-18}$ O3 + BPINENE = CO + TXCARB24 : $k = 2.70 \times 10^{-16} e^{-1270/T}$ OH + BENZENE = RA13O2 : $k = 1.10 \times 10^{-12} e^{-193/T}$ OH + BENZENE = RA13O2 : $k = 1.08 \times 10^{-12} e^{-190/T}$ OH + BENZENE = AROH14 + HO2 : $k = 1.23 \times 10^{-12} e^{-193/T}$ OH + BENZENE = AROH14 + HO2: $k = 1.22 \times 10^{-12} e^{-190/T}$ $OH + n-PrOH = EtCHO + HO2 : k = 2.71 \times 10^{-12}$ OH + n-PrOH = EtCHO + HO2: $k = 2.27 \times 10^{-12} e^{70/T}$ $OH + n-PrOH = RN9O2 : k = 2.82 \times 10^{-12}$ OH + n-PrOH = RN9O2 : $k = 2.33 \times 10^{-12} e^{70/T}$ $RU1002 + NO3 = CARB7 + HCHO + HO2 + NO2 : k = 5.00 \times 10^{-13}$ $RU10AO2 + NO3 = CARB7 + HO2 + CO + NO2 : k = 2.30 \times 10^{-13}$ HOCH2CO3 + HO2 = HOCH2CO3H : $k = 4.30 \times 10^{-13} e^{1040/T}$ HOCH2CO3 + HO2 = HOCH2CO3H : $k = 2.912 \times 10^{-13} e^{980/T}$ NRU14O2 + HO2 = NRU14OOH : $k = 2.24 \times 10^{-13} e^{1300/T}$ NRU14O2 + HO2 = NRU14OOH : $k = 2.05 \times 10^{-13} e^{1300/T}$

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388
          NRU12O2 + HO2 = NRU12OOH : k = 1.82 \times 10^{-13} e^{1300/T}
389
          NRU12O2 + HO2 = NRU12OOH : k = 2.05 \times 10^{-13} e^{1300/T}
390
391
          RTN26O2 + HO2 = RTN26OOH : k = 2.66 \times 10^{-13} e^{1300/T}
392
          RTN26O2 + HO2 = 0.56RTN26OOH + 0.44RTN25O2 + 0.44OH : k = 5.20 \times 10^{-13} e^{980/T}
393
394
          CH3O2 + RO2 = HCHO + HO2 : k = 6.01 \times 10^{-14} e^{416/T}
395
          CH3O2 + RO2 = HCHO : k = 6.01 \times 10^{-14} e^{416/T}
396
          CH3O2 + RO2 = MeOH : k = 6.01 \times 10^{-14} e^{416/T}
397
                                                                k_{CH302} = 1.03 \times 10^{-13} e^{365/T}
398
          CH3O2 + RO2 = HCHO + HO2 : 2*k_{CH3O2}*7.18*e^{-885/T}
399
          CH3O2 + RO2 = HCHO : 2*k_{CH3O2}*0.5*(1-7.18*e^{-885/T})
400
401
          CH3O2 + RO2 = CH3OH : 2^{k}k_{CH3O2}^{*0.5*(1-7.18*e^{-885/T})};
402
403
          RU14O2 + HO2 = RU14OOH : k = 2.24 \times 10^{-13} e^{1300/T}
404
          RU14O2 + HO2 = RU14OOH : k = 2.05 \times 10^{-13} e^{1300/T}
405
406
          RU14O2 + RO2 = UCARB12 + HO2 : k = 4.31 \times 10^{-13}
407
          RU14O2 + RO2 = UCARB12 + HO2 : k = 1.26 \times 10^{-13}
408
409
          RU14O2 + RO2 = UCARB10 + HCHO + HO2 : k = 1.28 \times 10^{-12}
410
          RU14O2 + RO2 = UCARB10 + HCHO + HO2 : k = 1.13 \times 10^{-12}
411
412
          RU12O2 + RO2 = MeCO3 + HOCH2CHO : k = 1.40 \times 10^{-12}
413
          RU12O2 + RO2 = MeCO3 + HOCH2CHO : k = 1.772 \times 10^{-13}
414
415
          RU12O2 + RO2 = HO2 + CARB7 + CARB3 : k = 6.00 \times 10^{-13}
416
          RU12O2 + RO2 = HO2 + CARB7 + CARB3 : k = 1.668 \times 10^{-13}
417
418
          RU10O2 + RO2 = MeCO3 + HOCH2CHO : k = 1.00 \times 10^{-12}
419
          RU1002 + RO2 = MeCO3 + HOCH2CHO : k = 1.28 \times 10^{-13}
420
421
          RU10O2 + RO2 = CARB6 + HCHO + HO2 : k = 6.00 \times 10^{-13}
422
          RU1002 + RO2 = CARB6 + HCHO + HO2 : k = 5.49 \times 10^{-13}
423
424
          RU10O2 + RO2 = CARB7 + CO + HO2 : k = 4.00 \times 10^{-13}
425
          RU10AO2 + RO2 = CARB7 + CO + HO2 : k = 3.60 \times 10^{-13}
426
427
          NRU12O2 + RO2 = NOA + CO + HO2 : k = 9.60 \times 10^{-13}
428
          NRU12O2 + RO2 = NOA + CO + HO2 : k = 4.80 \times 10^{-13}
429
430
          RTN26O2 + RO2 = RTN25O2 : k = 2.00 \times 10^{-12}
431
          RTN26O2 + RO2 = RTN25O2 : k = 1.00 \times 10^{-11}
432
433
          RTN26O2 + RO2 = RTN25O2 : k = 2.00 \times 10^{-12}
434
          RTN26O2 + RO2 = RTN25O2 : k = 1.00 \times 10^{-11}
435
436
          OH + CARB3 = CO + CO + HO2 : k = 1.14 \times 10^{-11}
437
          OH + CARB3 = CO + CO + HO2 : k = 2.48 \times 10^{-12}
438
439
          OH + CARB6 = MeCO3 + CO : k = 1.72 \times 10^{-11}
440
          OH + CARB6 = CO + CO + HO2 : k = 1.90 \times 10^{-12} e^{575/T}
441
442
          OH + NOA = CARB6 + NO2 : k = 1.30 \times 10^{-13}
443
          OH + NOA = CARB6 + NO2 : k = 6.70 \times 10^{-13}
444
```

445 446 447	OH + RU14NO3 = UCARB12 + NO2 : $k = 5.55 \times 10^{-11}$ OH + RU14NO3 = UCARB12 + NO2 : $k = 1.02 \times 10^{-11}$
448	$OH + RN8OOH = CARB6 + OH : k = 4.42 \times 10^{-12}$
449	$OH + RN8OOH = CARB6 + OH : k = 1.02 \times 10^{-11}$
450	
451	$RTN23O2 + NO = RTN23NO3 : k = 2.83 \times 10^{-13} e^{360/T}$
452	$RU12O2 + NO = RN12NO3 : k = 9.45 \times 10^{-14} e^{360/T}$
453	
454	$RTN23O2 + OH = Me2CO + TNCARB12 + NO2 : k = 5.37 \times 10^{-12}$
455	$TNCARB12 + OH - TNCARB11 + HO2 : k = 3.22 \times 10^{-12}$
456	$TNCARB11 + OH - RTN10O2 + HO2 : k = 1.33 \times 10^{-11}$
457	$\frac{\text{TNCARB11} + \text{NO3} - \text{RTN1002} + \text{CO} + \text{HONO2} : k - 7.92 \times 10^{-12} \text{e}^{-1862/T}}{\text{e}^{-1862/T}}$
458	

- 459 <u>Wet Deposition Parameters</u>

462 in CRI-STRAT (Archer-Nicholls et al., 2021)	461	Table S1 - New or updated wet deposition parameters. Text/figures in parentheses show values used
	462	in CRI-STRAT (Archer-Nicholls et al., 2021)

Species	Surrogate	Reference	k(298K)	$-\Delta H/R$
НОС2Н4ООН	HOC2H4OOH (EtOOH)	Schwantes et al (2020)	1.9e6 (3.4e2)	6.01e3 (5.70e3)
CARB7	Hydroxyacetone (Hydroxyacetone)	Schwantes et al (2020)	1.46e3 (1.4e2)	6.01e3 (5.70e3)
CARB10	Hydroxyacetone (Hydroxyacetone)	Schwantes et al (2020)	1.46e3 (1.4e2)	6.01e3 (5.70e3)
CARB13	Hydroxyacetone (Hydroxyacetone)	Schwantes et al (2020)	1.46e3 (1.4e2)	6.01e3 (5.70e3)
CARB16	Hydroxyacetone (Hydroxyacetone)	Schwantes et al (2020)	1.46e3 (1.4e2)	6.01e3 (5.70e3)
CARB3	Glyoxal (Methylglyoxal)	Schwantes et al (2020)	4.19e5 (3.5e3)	7.48e3 (7.2e3)
RA13NO3	RU14NO3 (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RA16NO3	RU14NO3 (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RA19NO3	RU14NO3 (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RN800H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RN1100H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)

RN14OOH	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RN17OOH	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RU14OOH	RU14OOH (EtOOH)	Schwantes et al (2020)	3.5e6 (3.4e2)	6.01e3 (5.70e3)
RU12OOH	MVKOOH (EtOOH)	Schwantes et al (2020)	1.24e6 (3.4e2)	6.01e3 (5.70e3)
RU10OOH	MVKOOH (EtOOH)	Schwantes et al (2020)	1.24e6 (3.4e2)	6.01e3 (5.70e3)
NRU14OOH	ISOPNOOH (EtOOH)	Schwantes et al (2020)	8.75e4 (3.4e2)	6.01e3 (5.70e3)
NRU12OOH	MVKN (EtOOH)	Schwantes et al (2020)	1.84e5 (3.4e2)	6.01e3 (5.70e3)
RN9OOH	HOC3H7OOH (EtOOH)	Schwantes et al (2020)	1.5e6 (3.4e2)	6.01e3 (5.70e3)
RA13OOH	BENZOOH (EtOOH)	Schwantes et al (2020)	2.3e3 (3.4e2)	6.01e3 (5.70e3)
RA16OOH	BENZOOH (EtOOH)	Schwantes et al (2020)	2.3e3 (3.4e2)	6.01e3 (5.70e3)
RA19OOH	BENZOOH (EtOOH)	Schwantes et al (2020)	2.3e3 (3.4e2)	6.01e3 (5.70e3)
RTN2800H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RTN26OOH	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RTN2500H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RTN1400H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RTX2800H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)

RTX2400H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e5 (3.4e2)	6.01e3 (5.70e3)
RTX2800H	Hydroperoxy acetone (EtOOH)	Schwantes et al (2020)	1.16e4 (3.4e2)	6.01e3 (5.70e3)
RTN26PAN	TERPA2PAN (no wet dep before)	Schwantes et al (2020)	9.59e3 (N/A)	6.01e3 (N/A)
RTN23NO3	Beta Isoprene hydroxy nitrate (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RN9NO3	HONITR (no wet dep before)	Schwantes et al (2020)	2.64e3 (N/A)	6.01e3 (N/A)
RN12NO3	HONITR (no wet dep before)	Schwantes et al (2020)	2.64e3 (N/A)	6.01e3 (N/A)
RN15NO3	HONITR (no wet dep before)	Schwantes et al (2020)	2.64e3 (N/A)	6.01e3 (N/A)
RN18NO3	HONITR (no wet dep before)	Schwantes et al (2020)	2.64e3 (N/A)	6.01e3 (N/A)
RU14NO3	Beta Isoprene hydroxy nitrate (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RTN28NO3	Beta Isoprene hydroxy nitrate (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RTN25NO3	Beta Isoprene hydroxy nitrate (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RTX28NO3	Beta Isoprene hydroxy nitrate (no wet dep before)	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)
RTX22NO3	Beta Isoprene hydroxy nitrate (no wet dep	Schwantes et al (2020)	8.34e3 (N/A)	6.01e3 (N/A)

	before)			
AROH14	Phenol (MeOH)	Schwantes et al (2020)	2.84e3 (2.3e2)	2.70e3 (4.9e3)
ARNOH14	Nitrophenol (MeOH)	Guo and Brimblecombe (2007)	8.5e1 (2.3e2)	6.27e3 (4.9e3)
AROH17	Phenol (MeOH)	Schwantes et al (2020)	5.67e2 (2.3e2)	5.80e3 (4.9e3)
ARNOH17	Nitrophenol (MeOH)	Guo and Brimblecombe (2007)	8.5e1 (2.3e2)	6.27e3 (4.9e3)
IEPOX	IEPOX (new species)	Schwantes et al (2020)	3.0e7 (N/A)	6.01e3 (N/A)
HMML	HMML (new species)	Schwantes et al (2020)	2.3e5 (N/A)	6.01e3 (N/A)
HUCARB9	Unsaturated hydroxy carbonyl (new species)	Schwantes et al (2020)	1.1e5 (N/A)	6.00e3 (N/A)
HPUCARB12	HPALD (new species)	Schwantes et al (2020)	2.3e5 (N/A)	6.01e3 (N/A)
DHPCARB9	DHPMPAL (new species)	Schwantes et al (2020)	9.37e7 (N/A)	6.01e3 (N/A)
DHPR1200H	DHPMPAL (new species)	Schwantes et al (2020)	9.37e7 (N/A)	6.01e3 (N/A)
DHCARB9	Hydroxy acetone (new species)	Schwantes et al (2020)	1.46e3 (N/A)	4.9e3 (N/A)
RU12NO3	MVKN (new species)	Schwantes et al (2020)	1.84e5 (N/A)	6.00e3 (N/A)
RU1NO3	MVKN (new species)	Schwantes et al (2020)	1.84e5 (N/A)	6.00e3 (N/A)

Table S2 - Emitted species and their sources. All biogenic emissions are 2011-201 MEGAN-MACCclimatologies and oceanic emissions are POET 1990 emissions.

Species	Source(s)
SO ₂	Natural, anthropogenic (surface and high)

DMS	Natural, biomass burning
C ₂ H ₄	Anthropogenic, biomass burning, biogenic, oceanic
C ₂ H ₆	Anthropogenic, biomass burning, biogenic, oceanic
C ₃ H ₆	Anthropogenic, biomass burning, biogenic, oceanic
C ₃ H ₈	Anthropogenic, biomass burning, biogenic, oceanic
C4H10	Anthropogenic, biomass burning, biogenic, oceanic
C ₅ H ₈	Biomass burning, biogenic
СО	Anthropogenic, biomass burning, biogenic, oceanic
EtCHO (propionaldehyde)	Anthropogenic, biomass burning, biogenic
EtOH	Anthropogenic, biomass burning, biogenic
НСНО	Anthropogenic, biomass burning, biogenic
HCOOH (methanoic acid)	Anthropogenic, biomass burning, biogenic
MEK (methyl ethyl ketone)	Anthropogenic, biomass burning, biogenic
Me ₂ CO (acetone)	Anthropogenic, biomass burning, biogenic
MeCHO (acetaldehyde)	Anthropogenic, biomass burning, biogenic
MeCO ₂ H (ethanoic acid)	Anthropogenic, biomass burning, biogenic
MeOH (methanol)	Anthropogenic, biomass burning, biogenic
TBUT2ENE (trans but-2-ene)	Anthropogenic, biomass burning, biogenic
Toluene	Anthropogenic, biomass burning, biogenic
NO	Anthropogenic, biomass burning, biogenic, soil
NH ₃	Anthropogenic, biomass burning, biogenic, oceanic
Alpha pinene	Biomass burning, biogenic
Beta pinene	Biomass burning, biogenic

Black Carbon	Biofuel, biomass burning (surface and high), fossil fuels
Benzene	Biomass burning, anthropogenic
C_2H_2	Biomass burning, anthropogenic
CH4 [*]	Biomass burning
HOCH ₂ CHO	Biomass burning
Organic carbon	Biofuel, biomass burning (surface and high), fossil fuels
Toluene	Biogenic, anthropogenic, biomass burning
Oxylene	Anthropogenic, biomass burning

* Lower boundary condition imposed in model

469

For the observation-model comparisons, the CS and CS2 runs used anthropogenic timeseries emissions
for all runs up to and including 2014 and 2014 timeslice emissions for the runs in 2016 due to a current
lack of post-2014 emissions for CRI. All emissions were based on the CMIP6 CEDS inventories (Hosely
et al. 2018). The ST runs used timeseries anthropogenic emissions based on the CMIP6 CEDS inventories
for all runs up to 2014 and then time series emissions based on SSP370 for runs in 2016.

475 476 477

478 <u>Section S2 Sensitivity Test Changes</u>479

480 CRI v2.2 reactions are shown in red, the changes made for each sensitivity test are shown in black. For 481 termolecular reactions, complex rate constants are used and in these cases the low pressure limit (k_0) , 482 high pressure limit (k_1) and F_c value are specified.

483	
484	CRI_v2_2_o1d
485	$O(1D) + H2O = OH + OH : k = 2.14 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
486 487	O(1D) + H2O = OH + OH : $k = 2.20 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
488	$O(1D) + N2 = OH + OH : k = 2.00 \times 10^{-11} e^{130/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
489 490	O(1D) + N2 = OH + OH : $k = 1.80 \times 10^{-10} e^{110/T}$ cm ³ molecules ⁻¹ s ⁻¹
491	$O(1D) + O2 = OH + OH : k = 3.20 \times 10^{-11} e^{67/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
492	$O(1D) + O2 = OH + OH : k = 3.20 \times 10^{-11} e^{70/T} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
493 494	
495 496	CRI_v2_2_inorgN
497	O(3P) + NO = NO2: $k_0 = 1 \times 10^{-31} [M] (T/300)^{-1.6}, k_1 = 5 \times 10^{-11} (T/300)^{-0.3} F_c = 0.85$
498 499	O(3P) + NO = NO2: $k_0 = 9 \times 10^{-32} [M] (T/300)^{-1.5}, k_1 = 3 \times 10^{-11} F_c = 0.6$
500	O(3P) + NO2 = NO3: $k_0 = 1.30 \times 10^{-31} [M] (T/300)^{-1.5}, k_1 = 2.30 \times 10^{-11} (T/300)^{0.24} F_c = 0.6$
501	O(3P) + NO2 = NO3: $k_0 = 9 \times 10^{-32} [M] (T/300)^{-2}, k_1 = 2.2 \times 10^{-11} F_c = 0.6$

502 503 HO2 + NO2 = HO2NO2: $k_0 = 1.40 \times 10^{-31} [M] (T/300)^{-3.1}, k_1 = 4.00 \times 10^{-12} F_c = 0.4$ 504 HO2 + NO2 = HO2NO2: $k_0 = 1.80 \times 10^{-31} [M] (T/300)^{-3.2}, k_1 = 4.70 \times 10^{-12} F_c = 0.6$ 505 506 OH + NO = HONO: $k_0 = 7.40 \times 10^{-31} [M] (T/300)^{-2.4}, k_1 = 3.30 \times 10^{-11} (T/300)^{-0.3} F_c = 0.81$ 507 OH + NO = HONO: $k_0 = 7.40 \times 10^{-31} [M] (T/300)^{-2.4}, k_1 = 3.30 \times 10^{-11} (T/300)^{-0.3} F_c = e^{-T/1420}$ 508 509 OH + NO2 = HONO2: $k_0 = 3.20 \times 10^{-30} [M] (T/300)^{-4.5}, k_1 = 3.00 \times 10^{-11} F_c = 0.41$ 510 OH + NO2 = HONO2: $k_0 = 2.60 \times 10^{-30} [M] (T/300)^{-3.2}, k_1 = 2.40 \times 10^{-11} (T/300)^{-1.3} F_c = 0.6$ 511 512 MeCO3 + NO2 = PAN: $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ 513 MeCO3 + NO2 = PAN: $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$ 514 515 EtCO3 + NO2 = PPAN: $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ 516 EtCO3 + NO2 = PPAN: $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$ 517 518 NO2 + NO3 = N2O5 : $k_0 = 3.60 \times 10^{-30} [M] (T/300)^{-4.10}$, $k_1 = 1.90 \times 10^{-12} (T/300)^{-0.2} F_c = 0.35$ 519 NO2 + NO3 = N2O5: $k_0 = 2.20 \times 10^{-30} [M] (T/300)^{-3.90}, k_1 = 1.50 \times 10^{-12} (T/300)^{-0.7} F_c = 0.60$ 520 521 HOCH2CO3 + NO2 = PHAN : $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ 522 HOCH2CO3 + NO2 = PHAN : $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$ 523 524 RTN2602 + NO2 = RTN26PAN : $k_0 = 2.368 \times 10^{-28} [M] (T/300)^{-6.50}$, $k_1 = 8.123 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ 525 RTN2602 + NO2 = RTN26PAN : $k_0 = 6.14 \times 10^{-29} [M] (T/300)^{-6.87}$, $k_1 = 7.94 \times 10^{-12} (T/300)^{-1.0} F_c = 0.60$ 526 527 Note that RU12PAN, which exists in CS but not in CS2, was not added back into the mechanism for this 528 test. In addition, the formation of MPAN, which involves RU1002+NO2 in CS but MACO3+NO2 in 529 CS2, was kept as MACO3+NO2 but the CS value of KFPAN was used. These changes are unlikely to 530 have a significant impact since PAN dominated the total concentration of all PAN-type species. 531 532 MACO3 + NO2 = MPAN : $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ 533 MACO3 + NO2 = MPAN : $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$ 534 535 HO2 + NO = OH + NO2 : $k = 3.45 \times 10^{-12} e^{270/T}$ 536 $HO2 + NO = OH + NO2 : k = 3.60 \times 10^{-12} e^{270/T}$ 537 538 OH + HO2NO2 = H2O + NO2 + O2 : $k = 3.20 \times 10^{-13} e^{690/T}$ 539 $OH + HO2NO2 = H2O + NO2 + O2 : k = 1.90 \times 10^{-12} e^{270/T}$ 540 541 $OH + PAN = HCHO + CO + NO2 : k = 3.40 \times 10^{-14}$ 542 OH + PAN = HCHO + CO + NO2 : $k = 9.50 \times 10^{-13} e^{-650/T}$ 543 544 $OH + MPAN = CARB7 + CO + NO2 : k = 6.38 \times 10^{-12}$ 545 $OH + MPAN = CARB7 + CO + NO2 : k = 3.60 \times 10^{-12}$ 546 547 OH + MeONO2 = HCHO + NO2 + H2O: $k = 4.00 \times 10^{-13} e^{-845/T}$ 548 549 OH + MeONO2 = HCHO + NO2 + H2O: $k = 1.00 \times 10^{-14} e^{-1060/T}$ 550 MeOO + NO = HCHO + NO2 + HO2: $k = 2.298 \times 10^{-12} e^{-360/T}$ 551 MeOO + NO = HCHO + NO2 + HO2: $k = 3.00 \times 10^{-12} e^{-280/T}$ 552 MeOO + NO = MeONO2 : $k = 2.30 \times 10^{-15} e^{-360/T}$ 553 554 MeOO + NO = MeONO2 : $k = 3.00 \times 10^{-15} e^{-280/T}$ 555 556 MeOO + NO3 = HO2 + HCHO + NO2 : $k = 1.20 \times 10^{-12}$

560

MeOO + NO = HO2 + HCHO + NO2 : $k = 1.00 \times 10^{-12}$

559 CRI v2 2 isoprene

561 In this branch, changes were made to the isoprene oxidation scheme to bring it as close as was practicable 562 to that used in CRI-STRAT. The major changes were the removal of the isomerisation reactions of the 563 isoprene peroxy radical, RU14O2, and the updated oxidation pathway of the species UCARB10 which 564 represents the major isoprene oxidation products methacrolein (MACR) and methyl vinyl ketone (MVK). 565 566 In this branch RU14O2 only underwent reactions with HO2, NO, NO3 and RO2. This meant the 567 production of 10 of the 12 new CRI v2.2 species (IEPOX, HMML, HPUCARB12, HUCARB9, 568 DHPR12OOH, DHPCARB9, DHCARB9, MACO3, DHPR12O2 and RU10AO2) and their subsequent 569 reactions, which are key in the HOx-recycling process, were removed from the mechanism. Note that the

570 production of two new organonitrate species, RU12NO3 and RU10NO3, and their subsequent reaction

571

were maintained as these had much less to do with the HOx-recycling feature under examination. It 572

should also be noted that where there was a difference between the rate constants in CS and CS2 for a 573 given reaction (e.g. changes in the RO2+NO and RO2+NO3 rate constants), the rate constant from CRI

574 v2.2 was used to minimise the other drivers for difference that was observed between this branch and the

575 full CRI v2.2 branch.

576

578

577 In addition, all isoprene oxidation reactions with OH, O3 and NO3 were reverted to those in CS.

```
579
           NO3 + C5H8 = NRU14O2 : k = 3.15 \times 10^{-12} e^{-450/T}
580
           NO3 + C5H8 = NRU14O2 : k = 3.0 \times 10^{-12} e^{-466/T}
581
582
           O3 + C5H8 = UCARB10 + CO + HO2 + OH : k = 1.288 \times 10^{-15} e^{-1995/T}
583
           O3 + C5H8 = HCHO + MeOO + CO + HO2 : k = 9.79 \times 10^{-16} e^{-1995/T}
584
           O3 + C5H8 = UCARB10 + HCOOH : k = 1.80 \times 10^{-15} e^{-1995/T}
585
           O3 + C5H8 = UCARB10 + HCHO + H2O2 : k = 3.97 \times 10^{-15} e^{-1995/T}
           O3 + C5H8 = MeCO3 + HCHO + CO + OH : k = 1.29 \times 10^{-15} e^{-1995/T}
586
           O3 + C5H8 = UCARB10 + CO : k = 9.785 \times 10^{-16} e^{-1995/T}
587
           O3 + C5H8 = UCARB10 + CO + HO2 + OH : k = 2.12 \times 10^{-15} e^{-19/3/T}
588
589
           O3 + C5H8 = UCARB10 + HCOOH : k = 5.74 \times 10^{-15} e^{-1913/T}
590
591
           OH + C5H8 = RU14O2 : k = 2.70 \times 10^{-12} e^{390/T}
592
           OH + C5H8 = RU14O2 : k = 2.54 \times 10^{-12} e^{410/T}
593
594
           OH + UCARB10 = RU10O2 : k = 3.84 \times 10^{-12} e^{533/T}
595
           OH + UCARB10 = RU10O2 : k = 2.50 \times 10^{-11}
596
597
           NO3 + UCARB10 = RU10O2 + HONO2: k = 5.98 \times 10^{-13} e^{-1862/T}
598
           NO3 + UCARB10 = RU10O2 + HONO2 : k = 1.44 \times 10^{-12} e^{-1862/T}
599
600
           O3 + UCARB10 = HCHO + MeCO3 + CO + OH : k = 3.84 \times 10^{-16} e^{-1710/T}
601
           O3 + UCARB10 = HCHO + MeCO3 + CO + OH : k = 1.68 \times 10^{-18}
602
603
           O3 + UCARB10 = HCHO + CARB6 : k = 8.16 \times 10^{-16} e^{-1710/T}
604
           O3 + UCARB10 = HCHO + CARB6 + H2O2 : k = 1.17 \times 10^{-18}
605
606
           OH + UCARB12 = RU10O2 : k = 6.42 \times 10^{-11}
607
           OH + UCARB12 = RU10O2 : k = 4.52 \times 10^{-11}
```

NO3 + UCARB12 = RU10O2 : $k = 6.42 \times 10^{-11}$ NO3 + UCARB12 = RU10O2 : $k = 4.52 \times 10^{-11}$ O3 + UCARB12 = HOCH2CHO + MeCO3 + CARB3 + OH : $k = 6.00 \times 10^{-18}$ $O3 + UCARB12 = HOCH2CHO + MeCO3 + CO + OH : k = 2.14 \times 10^{-17}$ $O3 + UCARB12 = CARB6 + CO + OH + HO2 : k = 1.20 \times 10^{-17}$ O3 + UCARB12 = HOCH2CHO + CARB6 + H2O2 : $k = 2.64 \times 10^{-18}$ UCARB12 = MeCO3 + HOCH2CHO + CO + HO2:0.25 * jmacr UCARB12 = MeCO3 + HOCH2CHO + CO + HO2: jmacr UCARB12 = RU12O2 + HO2:0.5 * jmacr No replacement UCARB12 = RU12O2 + CARB7 + CO :0.25 * *jmacr* No replacement NRU12OOH = NOA + CARB3 + HO2 + OH: *jhmp* NRU12OOH = NOA + CO + HO2 + OH : jhmpNUCARB12 = HUCARB9 + CO + NO2 + OH: *jmacr* NUCARB12 = NOA + 2*CO + 2*HO2 : jmacr NUCARB12 = CARB7 + CO + HO2 + NO2:8 * jnoa No replacement All reactions of HUCARB9, HPUCARB12, DHCARB9, DHPCARB9, RU10AO2, MACO3, DHPR12O2, DHPR12OOH and IEPOX and HMML were removed. Reactions which produced these species reverted to their CS equivalents. OH + RU14OOH = 0.09UCARB12 + 0.94OH + 0.85IEPOX + 0.06RU14O2: $k = 7.14 \times 10^{-11}$ OH + RU14OOH = UCARB12 + OH: $k = 7.51 \times 10^{-11}$ OH + RU12OOH = RU10OOH + CO + HO2: $k = 3.50 \times 10^{-11}$ OH + RU12OOH = RU12O2: $k = 3.00 \times 10^{-11}$ OH + RU10OOH = CARB7 + CO + OH: $k = 3.84 \times 10^{-11}$ OH + RU10OOH = RU10O2: $k = 3.00 \times 10^{-11}$ MPAN + OH = HMML + NO3: $k = 2.262 \times 10^{-11}$ No replacement MPAN = MACO3 + NO2: $k = 1.60 \times 10^{16} e^{-13500/T}$ MPAN = RU1002 + NO2: $k_0 = 1.10 \times 10^{-5} e^{-10100/T}$, $k_1 = 1.90 \times 10^{17} e^{-14100/T}$ $F_c = 0.30$ MACO3 + NO2 = MPAN : $k_0 = 3.28 \times 10^{-28} [M] (T/300)^{-6.87}, k_1 = 1.125 \times 10^{-11} (T/300)^{-1.105} F_c = 0.30$ MACO3 + NO2 = MPAN : $k_0 = 8.50 \times 10^{-29} [M] (T/300)^{-6.50}, k_1 = 1.10 \times 10^{-11} (T/300)^{-1.0} F_c = 0.60$ RU14O2 = UCARB10 + HCHO + OH No replacement RU14O2 = 0.5 HPUCARB12 + 0.5 HO2 + 0.5 DHPR12O2 No replacement RU10AO2 + NO3 = CARB7 + HCHO + HO2 + NO2 : $k = 2.30 \times 10^{-12}$ RU10O2 + NO3 = CARB7 + HCHO + HO2 + NO2 : $k = 5.00 \times 10^{-13}$ RU10AO2 + RO2 = CARB7 + CO + HO2 : $k = 3.60 \times 10^{-13}$

```
RU10O2 + RO2 = CARB7 + HCHO + HO2 : k = 4.00 \times 10^{-13}
RU12O2/RU10O2 - aside from changes from RU10AO2 to RU10O2, no other changes made
```

CRI v2 2 RO2 N

The only change made to the mechanism for this test was reversion of the rate constants of RO2 with NO and NO3. Where branching ratios had changed between CS and CS2, the CRI v2.2 were maintained with rate constants scaled accordingly. The red rate constants below were changed to those in black:

```
kRO2NO: k = 2.70 \times 10^{-12} e^{360/T}
kRO2NO: k = 2.40 \times 10^{-12} e^{360/T}
```

kRO2NO3: $k = 2.30 \times 10^{-12}$ kRO2NO:3 $k = 2.50 \times 10^{-12}$

Five acyl peroxy species in CRI featured a different RO2 + NO rate constant, kAPNO, which decreased by 7.5% in CRI v2.2.

kAPNO: $k = 7.50 \times 10^{-12} e^{290/T}$ kAPNO:3 $k = 8.10 \times 10^{-12} e^{290/T}$

Section S3 iBVOC and Megan-MACC Emissions

693 The difference between two possible BVOC emissions approaches, the iBVOC approach and the non-694 interactive MEGAN-MACC emission approach, was considered. Globally, the annual average noninteractive isoprene emissions were 5.9% higher (576.9 Tg yr⁻¹ vs. 545.0 Tg yr⁻¹) while MT emissions 695 were 29% lower (97.5 Tg yr⁻¹ v. 137.3 Tg yr⁻¹, cf 95±3 Tg yr⁻¹ Sindelarova et al., 2014) (Fig. S1). 696 697 Emissions at three of the surface observational sites, ATTO, Z2F and Borneo, were also compared with a 698 specific focus on the months where model-observational comparisons were performed. At the ATTO and 699 Z2F sites monthly MEGAN-MACC isoprene emissions were lower than iBVOC emissions ($\sim 40\%$ for 700 the months considered). Non-interactive MT emissions at the ATTO sites were also lower than iBVOC 701 emissions (35% Feb and 25% Sept) but slightly higher in June for the Z2F site. In Borneo, MEGAN-702 MACC isoprene and MT emissions were ~25% and ~15% lower than iBVOC over the April-July period 703 respectively.

704

705 A spatial comparison of the emission approaches was also performed (Fig. S2). Annually averaged,

706 iBVOC exhibited greater isoprene emissions in the northern part of South America but lower emissions at

707 more southern latitudes as well as general southern migration of isoprene emissions in Africa. Isoprene

708 emissions in Australia were significantly lower. These differences were more pronounced in the June-

709 July-August (JJA) period while in the December-January-February (DJF) period iBVOC also exhibited

710 increased emissions over China and South East Asia and the northern hemisphere boreal forests but lower

711 emissions over the South East USA. For monoterpenes, iBVOC simulated greater JJA emissions in the

712 boreal forest, South East USA and South East Asia and greater DJF emissions in much of South America.







- 719 2005-2013). Emissions per unit area for isoprene and MT at the ATTO (c, d), Bannan (e, f) and
- 720 Borneo (g, h) observational sites. Black dots indicate months when model-observational
- 721 comparisons were performed at the corresponding site.
- 722





Figure S2. Difference in emissions between the iBVOC and MEGAN-MACC 2001-2010
climatologies (MM) emission approaches for isoprene and monoterpenes. Annual average (top panels), DJF average (middle panels) and JJA average (lower panels).



Figure S3. Location of the two in-situ Amazon observation sites (Bannan and ATTO), city of
 Manuas and GABRIEL aircraft campaign paths (upper left), OP3 observation tower and FAAM
 aircraft campaign flights over Borneo (upper right) and SEAC⁴RS flight campaign over the South

Fight Campaign Inglits over Borneo (upper Fight) and SEAC RS inglit campaign over the South
 East USA (lower). Map Sources: Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX,
 Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Table S3 – Additional information regarding observational data

Dataset	Notes		
SE4C ⁴ RS	All data points below limit of detection set to zero		
GABRIEL	Estimated LODs: Isoprene 0.1 ppb, MVK 0.09 ppb, Acetone 0.09 ppb		
	Non-zero data points below the LOD were not removed.		
FAAM	Estimated LOD: Isoprene 0.1 ppb		
	Data marked as low quality was ignored		
Borneo	Data marked as low quality was ignored		
ATTO	Monoterpene LOD: 0.05 ppb (Sept 2013) 0.06 ppb (March 2014)		
	Isoprene LOD: 0.09 ppb (Feb 2013), 0.1 ppb (Sept 2013)		
	Acetone LOD: 0.03 ppb (Feb 2013), 0.05 ppb (Sept 2013)		
	Isoprene oxidation products LOD: 0.13 ppb (Feb 2013), 0.07 ppb (Sept 2013)		

LOD estimated as 2σ of the background average. Non-zero data points below the
LOD were not removed.

740 Section S4 Overview of field Brazil ZF2 measurements

740

742 A suite of online measurement techniques was deployed in Central Amazonia, at the ZF2 site located 61 743 km north upwind of Manaus (60°11'W, 2°5'S) in June and July 2016. This is a site that at the transition 744 between wet and dry seasons that is mostly influenced by natural biogenic emissions, with virtually no 745 biomass burning and no anthropogenic pollution at the time of experiment. A high-resolution TOF-CIMS 746 using iodide-adduct ionization was coupled to an Aerodyne Research Incorporated FIGAERO (Lee et al., 747 2014, Lopez-Hilfiker et al., 2015, Bannan et al., 2019), and was utilized for the semi-simultaneous 748 measurement of a range of oxygenated species in the gas and particle phase. An Aerodyne ACSM 749 (Aerosol Chemical Speciation Monitor) monitored the bulk submicron organic and inorganic aerosol 750 composition and a PTR-MS (proton transfer reaction mass spectrometer) was used to measure isoprene 751 and a subset of isoprene oxidation products. Routine measurements including NO_x , SO_2 and O_3 and key 752 meteorological conditions were also made. Further details of all aspects of the field measurements are 753 given in the sections that follow. 754

755 TOF-CIMS technique

- 756 *Configuration and operating technique*
- 757

758 The gas-phase measurements of the Manchester time-of-flight chemical ionization mass spectrometer 759 (TOF-CIMS) instrument have been described in detail previously (Priestley et al, 2015) but the specific 760 setup and operation procedures used in the present work is described herein. The instrument comprises an 761 Aerodyne FIGAERO inlet attached to a reduced pressure ion molecule reaction (IMR) region in front of a 762 Tofwerk atmospheric pressure interface high resolution time-of-flight mass spectrometer (Lopez-Hilfiker 763 et al., 2015) together these facilitate simultaneous gas and particle phase measurements. In the present work, a Tofwerk X-Ray ionization source was used in place of the Po-210 source normally used with 764 765 iodine CIMS. The instrument performance was tracked daily by monitoring the baseline, single ion signal 766 measurements, m/z calibrations, regular gas-phase calibrations and high-frequency filter and gas-phase 767 background measurements.

768

The Aerodyne FIGAERO is a two-port inlet with the first dedicated to gas sampling (PFA Teflon tubing, 20 SLM measured flow rate) and the second to aerosol sampling (stainless steel inlet, 10 SLM measured flow rate). The sampling lines were situated at an altitude just above the canopy to avoid sampling being compromised by trees or structures. Recently, Liu *et al. (2016)* discussed in detail the effect of inlets on species quantification - the inlets used in the present work were chosen due to the limitations of the measurement site.

775

The FIGAERO couples both inlets with the chemical ionization region of the mass spectrometer and
operates in two modes: (A) ambient air sampling for trace gas analysis using CIMS and simultaneous
particle collection on a PFTE filter via a separate inlet, and, (B) thermal desorption of the collected
particles in nitrogen, allowing detection of the desorbed vapors via CIMS.

780

The IMR was held at a constant pressure by a scroll pump (Agilent SH-112), regulated with a servo
control valve placed between the scroll pump and IMR. The ionizing reagent, I-, was generated via X-ray
ionization of CH₃I. 10 sccm of N₂ was flowed over a methyl iodide (CH₃I) permeation tube (held at 40°C)
and the resultant CH₃I-entrained N₂ carried by a 2 SLM N₂ flow through the X-ray ionizer into the IMR,

orthogonally to the sample flow. The ionizer and ambient air flows were allowed to mix, such that trace

786 chemical species within the ambient air sample were ionized by I-, generating iodine adducts. The

- resultant flow was sampled via a critical orifice into the first of four differentially pumped chambers in
- the TOF-CIMS. The first chamber was held at a set pressure (1.6 mbar) by a scroll pump (Triscroll 600)

and the subsequent chambers were pumped by a split flow turbo molecular drag pump. Quadrupole ion
guides transmitted the ions through these chambers while simultaneously providing additional collisional
cooling and energetic homogenization of the ions as they entered the extractor region. The electric fields
were set to optimize the total ion signal and transmission of the iodide adducts.

793

795

794 *CIMS Calibrations and background measurements*

Mass calibration was performed using 5 known masses (I⁻, I⁻.H₂O, I⁻.HCOOH, I₂⁻ and I₃⁻) that cover a range of m/z 127 to 380. The mass calibration was fitted by a 3rd order polynomial and was accurate to within 1 ppm, ensuring peak identification for all species was accurate below 1 ppm. The Tofwarespecific FIGAERO-CIMS analysis software (version 3.1) was utilized to attain high-resolution 1Hz time series of all of the species identified here, in both the gas- and particle-phases. Further analysis was done using software developed in-house.

Gas-phase background measurements were made once every 30 minutes for 30 seconds by overflowing
the IMR just above the pinhole with wetted high-purity nitrogen. Data was background-subtracted using
an interpolation of the two background measurements recorded either-side of data collection. An example
of the data processing for an arbitrary mass is shown in Figure S1.

807



808 809

Fig. S4 Retrieval of background-corrected data from raw data for a subset of the measurement campaign
for an arbitrary mass. The background counts obtained during the background period (blue dots) are

812 interpolated to yield the interpolated background data (orange line). This is subtracted from the raw signal

813 (red line) to obtain the corrected measurement (black line). All data are in units of counts per second814 (CPS).

815

Background filter measurements comprised a ramp, soak and cool cycle matching that of the ambient air
sampling method. Each background measurement was applied to the thermogram measurements made
until the next background filter measurement was recorded. In the event of a break in FIGAERO-CIMS
measurements (i.e., due to temporary failure or power shortages), a new filter was placed into the
instrument. The new filter was cleaned by ramping the temperature to 200°C for a duration of 20 mins
and subsequently cooled, with a complete cycle immediately after. Where there was no break in the

- measurements for ~2 days, the cleaning process was undertaken for the existing installed filter. Detailed
 analysis during the measurements was undertaken to ensure that all of the collected material was being
 volatilized during normal operation.
- 825

826 Offline calibrations after the field work campaign were performed specific to the isoprene oxidation

- species that were observed at the ZF2 site. 2-Methyltetrols, 2-methylglyceric acid, and IEPOX weresynthesized by the University of North Carolina, Department of Environmental Sciences & Engineering
- 829 according to procedures outline in Bondy et al. (2018), Budisulistiorini et al. (2015), and Zhang et al.
- 830 (2012), respectively. These standards were dissolved in acetone at known concentrations and using a
- 831 micro-syringe were deposited on the FIGAERO filter and thermally desorbed using a known continuous
- 832 flow of nitrogen over the filter. This was performed following the methodology devised in Lee et al.
- 833 (2014). The measured sensitivities for $C_5H_{10}O_3$, $C_4H_8O_4$, $C_5H_{12}O_4$ varied by a maximum of 25% from each other with the mean sensitivity of the 3 isoprene oxidation standards being only 8% higher than that of
- 835 acetic acid. The mean sensitivity of the 3 isoprene oxidation standards in the gas and particle phase is 836 therefore applied to the full data set presented here.
- All species sensitivities reported herein were deduced assuming a linear response between reported and
- formic acid calibrations in the field (where day-to-day calibrations were performed) and the laboratory. A
- range of other species were calibrated for after the campaign, and relative calibration factors were derived
- using the measured formic acid sensitivity during these calibrations, as has been performed previously $(L \circ Preton et al. 2018)$.
- 841 (Le Breton *et al.*, 2018; Bannan et al., 2015)
- 842
- 843 Supporting measurements
- 844

845 Several supporting measurements were made that allow for interpretation of the TOF-CIMS

- 846 measurements. These include gas-phase measurements of biogenic volatile organic compounds (BVOCs)
- from a proton transfer time-of-flight mass spectrometer (PTR-ToF-MS; Ionicon Analytik) and particlephase measurements using an aerosol chemical speciation monitor (ACSM)(DeCarlo *et al.*, 2006).
- 849 Operation and analysis procedures are outlined elsewhere for the PTR-TOFMS (Liu *et al.*, 2016) and for
- the ACSM (de Sá *et al.*, 2017). The chemical composition of submicrometer aerosols was measured on-
- 851 line by mass spectrometry using an Aerosol Chemical Speciation Monitor (ACSM). The aerosol mass
 852 spectrometer was used to characterize a wide range of non-refractory sub-micron aerosol particles such as
- 853 organics, nitrate, sulfate, ammonium, and chloride in real-time with time-resolution of <15 minutes. Sulfur dioxide, NO_x and O₃ mixing ratios were monitored at both sites using trace gas analyzers (Thermo
- 43i-TLE, Thermo 42i and Thermo 49i, respectively). Meteorological parameters were measured using
- two different automatic weather stations (HOBO U30 Station GSM-UDP). Meteorological measurements comprised: temperature (\pm 0.3 °C), humidity (\pm 3–5%), rain amount (\pm 5% for daily accumulation), wind
- speed (0.3–0.5 ms-1) and direction (\pm 3°), where the resolution and accuracy are stated in parenthesis.
- 859
- 860
- 861
- 862
- 863
- 864





Figure S5 - Monthly mean ozone from observations (black) and CS (cc297 upper plot, red) and CS2
(cc298 lower plot, red) runs at 10 sites and 4 pressure levels (250 hPa – 1st row, 500 hPa – 2nd row,
700 hPa – 3rd row, 900 hPa – 4th row).

872

873



Figure S6 - Median observed and model (CS2) concentrations for (a) O₃, (b) CO, (c) Isoprene
nitrate, (d) NO₂ from the SEAC⁴RS flight campaign. Panels (e) and (f) show median observed NO
(GABRIEL) and NO₂ (FAAM) concentrations from observations and all mechanisms. Shading
shows IQR.

- 880
- 881 <u>Section S5 Other Species</u>
- 882
- 883 CO
- As discussed in the context of HO_x, Borneo modelled surface CO was high biased for all mechanisms
- 885 (Fig. S7) with CS and CS2 exhibiting a bias 50-60 ppb in July when observations were low (~100 ppb)
- and ST a bias of 27 ppb. ST and CS were low and high biased respectively by around 13 ppb while CS2
- 887 was high biased by 27 ppb (Fig. S10). Over the Amazon CS and CS2 exhibit a smaller low bias than ST

888 while over Borneo, ST and CS perform well with ST high biased by 10-15 ppb (Fig. 3). The CO profile

- 890

891 Monthly mean surface CO from the longer CS2 runs show a consistent increase across multiple locations

in CO concentration compared to CS but, due to the spatially-varying performance of CS (high bias in

- 893 certain regions and low bias in others), CS2 appeared no better or worse than CS on a global scale. A
- small increase in low altitude CO was also seen in the annual mean CO vertical profiles.

896 HONO₂

897 Tropospheric vertical profiles of annual mean nitric acid at multiple locations show a small increase in 898 CS2 in a few locations ($<\sim$ 50 ppt) relative to CS, slightly increasing the general model high bias. In the 899 stratosphere, HONO₂ was slightly (0.25-0.5 ppb) lower than CS in the 20-30 km increasing the model low 900 bias.

901

902 Benzene and SO₂

In the Amazon CS and CS2 show reasonable agreement for benzene while all mechanisms have a daytimelow bias for SO₂ (Fig. S10).

905

906 PAN

PAN is high biased in Borneo (Fig S7), with CS and CS2 worse than ST. The increase in PAN in CS is
documented by Archer-Nicholls et al (2021) and the general reduction from CS to CS2 is discussed in
Section 4.

910

911 HCHO

912 The model high bias for HCHO in Borneo (Fig. S7) increased from ST to the CS due to additional

913 secondary production (Archer-Nicholls et al., 2021) while above the Amazon, CS2 (Fig. S10) did yield an

914 improvement relative to CS at low altitudes (< 1km). The general reduction in HCHO in CS2 relative to

- 915 CS is discussed further in Section 5.
- 916

917 Acetone and Acetaldehyde

918 All mechanisms are significantly high biased for acetone and acetaldehyde in Borneo and for acetone in

919 the Amazon (Figs S7, S8). Above the Amazon, the three mechanisms are broadly similar for acetone

920 displaying high bias at low altitude (greatest in the CRI mechanisms due to enhanced secondary

921 production) and much smaller bias above ~ 2km. This highlights the importance of the ongoing work to

922 update the photolysis of acetone and acetaldehyde species. These updates which are yet to be incorporated

923 in UKCA have been noted to increase acetone photolysis frequency by 3-5x in the lowest 5km (Prather et

- al., 2013) and so should help to reduce model high bias.
- 925



- 928 Figure S7 Mean modelled (ST, CS and CS2) and observed diurnal profiles of HO₂, CO, HCHO,
- 929 Acetone, MeCHO, PAN and NO₂ profiles from Borneo. Observations are from the OP3 tower (ref)
- 930 and model output from the most relevant grid cell. Shading indicates ±1 standard deviation from
- 931 the mean and the numbers in **bold** show the mean diurnal model bias (model observations) for
- 932 species/locations where observations were recorded.
- 933
- 934
- 935







941 periods are taken as 9:00-15:00 and 21:00-03:00 respectively. Shaded regions indicate ± 1 standard

942 deviation from the mean.

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946

947 Figure S9 - Mean vertical profiles of isoprene oxidation products (here defined as the sum of

948 methacrolein, methyl vinyl ketone and ISOPOOH) and the ratio of isoprene oxidation products to

isoprene from observations taken at the ATTO tower (Yanez-Serrano et al., 2015) and model
output from ST, CS and CS2. Daytime and nighttime periods are taken as 9:00-15:00 and 21:00-

951 03:00 respectively. Shaded regions indicate ± 1 standard deviation from the mean.





955 Figure S10 - Mean modelled (ST, CS and CS2) and observed diurnal profiles of CO, NO2, Benzene

- and SO2 from the Bannan site in the Amazon. Shading indicates ±1 standard deviation from the
- 957 observation mean and the numbers in bold show the mean diurnal model bias (model -
- 958 observations). (Note that the ST mechanism does include benzene as a species.).



Figure S11. Mean modelled (ST, CS, CS2) and observed diurnal profiles of acetone, isoprene
oxidation products (here defined as the sum methacrolein, methyl vinyl ketone and ISOPOOH) at

966 the ATTO tower. Observations are from the OP3 tower (e.g. Hewitt et al., 2010, Table 3) and model

967 output from the most relevant grid cell. Shading indicates ±1 standard deviation from the

968 observation mean and the numbers in bold show the mean diurnal model bias (model -

observations).



Figure S12. Zonal mean change in ozone mixing ratio for 2006 for CS2 and CS (top left), CS2 and
the respective sensitivity tests and the sum of the changes from the sensitivity tests. The purple line
shows the mean tropopause height.

O_3 Lowest 500 m



982 983

Figure S13. Mean change in ozone mixing ratio for the lowest ~500 m for 2006 for CS2 and CS (top
left), CS2 and the respective sensitivity tests and the sum of the changes from the sensitivity tests.



990 Figure S14. Tropospheric zonal mean change in the major production and loss Ox fluxes for CS2 -

991 CS. These fluxes make up over 99% and 95% of total production and loss fluxes, respectively.





Figure S15. Mean change in OH concentration for the lowest ~500 m for 2006 for CS2 and CS (top left), CS2 and the respective sensitivity tests and the sum of the changes from the sensitivity tests.



- 1005

Figure S16. Tropospheric zonal mean change in OH for 2006 for CS2 and CS (top left), CS2 and the respective sensitivity tests and the sum of the changes from the sensitivity tests. The purple line shows the mean tropopause height.



- 1014

Figure S17. Zonal mean change in NOx for CS2 and CS (top left), CS2 and the respective sensitivity

- tests and the sum of the changes from the sensitivity tests. The purple line shows the mean
- tropopause height.



- 1021

Figure S18. Tropospheric zonal mean change in PANs for CS2 and CS (top left), CS2 and the respective sensitivity tests and the sum of the changes from the sensitivity tests. The purple line shows the mean tropopause height.



Figure S19. Zonal mean change in HONO₂ for CS2 and CS (top left), CS2 and the respective
sensitivity tests and the sum of the changes from the sensitivity tests. The purple line shows the
mean tropopause height.



1046 Figure S20. Zonal mean change in RONO₂ for CS2 and CS (top left), CS2 and the respective

sensitivity tests and the sum of the changes from the sensitivity tests. The purple line shows the
mean tropopause height.

Table S3 - Annual mean Ox diagnostics for CS, CS2 and sensitivity tests. Note that these data refer
 to the single year of analysis used for the sensitivity tests rather than the 4 year mean as in Table 4
 so the absolute values for CS and CS2 may differ from Table 4.

	CS	CS2	CRI_v2_2_0 1D	CRI_v2_2_ino rgN	CRI_v2_2_isop rene	CRI_v2_2_RO2 _N
O ₃ Burden (Tg)	324	351	334	334	353	345
O _x Lifetime (days)	17.23	18.63	17.28	18.73	18.62	18.61
Chemical Production (Tg year ⁻¹)	6579	6585	6780	6217	6650	6478

$HO_2 + NO$	4100	4231	4347	4009	4200	4165
MeOO + NO	1575	1585	1659	1468	1565	1549
$NO + RO_2$	852	720	721	694	833	718
Other	51	49	52	47	52	46
Chemical Loss (Tg year ⁻ ¹)	5837	5761	6003	5446	5828	5669
$O(^{1}D) + H_{2}O$	3168	2939	3221	2830	2956	2906
$HO_2 + O_3$	1659	1812	1760	1700	1814	1781
$OH + O_3$	739	796	809	711	785	772
O ₃ + Alkene	167	101	94	100	162	99
Other	105	113	109	104	112	110
Deposition (Tg year ⁻¹)	1129	1202	1155	1155	1200	1183

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1057 <u>Section S5</u>

1058 CO

1059 The CO burden increased by 3.2% from 343 Tg in CS to 354 Tg in CS2 with gains of 4-5 ppb in the SH 1060 low altitudes and 2-4 ppb in much of the troposphere (Fig. 10). Tropospheric destruction of CO by OH 1061 increased by 3.2% (~100 Tg yr⁻¹) with increases of 5-10% in the tropical and midlatitude PBL driven by 1062 the enhanced oxidising capacity and greater CO production. However, this increased destruction was 1063 outweighed by a 4.4% increase in chemical production, driven primarily by the updates to the isoprene 1064 scheme, illustrated by the large column increases occurring over the regions with high BVOC emissions 1065 (Fig. S26).

1066 1067

Table S4 - Annual mean CO diagnostics for CS and CS2.

	CRI-STRAT	CRI-STRAT 2
CO burden / Tg	326.8	337.9

CO lifetime / days	38.1	38.3
Production / Tg CO year ⁻¹	3227.5	3326.7
Emissions / Tg CO year ⁻¹	1110.2	1110.7
$HCHO + OH/NO_3 / Tg CO year^{-1}$	589.3	555.3
HCHO + hv / Tg CO year ⁻¹	1228.6	1239.4
Other Chemistry / Tg CO year ⁻¹	86.2	179.7
Other Photolysis / Tg CO year ⁻¹	213.1	242.2
Loss / Tg CO year ⁻¹	3158.2	3254.2
CO + OH / Tg CO year ⁻¹	2994.6	3086.6
CO Dry Dep / Tg CO year ⁻¹	163.6	167.6
Net production / Tg CO year ⁻¹	69.3	72.5

1069

1070 НСНО

1071 The HCHO burden decreased by 10% in CS2 (1.20 Tg to 1.08 Tg), driven primarily by the change to

1072 isoprene chemistry with a small contribution from the increased HCHO photolysis flux. Added

1073 competition from ISOPO2 isomerisation leads to the production of methylglyoxal (CARB6) and hydroxy

acetone (CARB7), at the expense of methacrolein and methyl vinyl ketone (lumped together as

1075 UCARB10). The former species tend to produce less HCHO than the latter, resulting in the greatest

1076 reduction in HCHO column over the regions with the greatest biogenic emissions (Fig. S26).



Figure S21. Annual zonal mean changes in (a) CO and (b) HCHO and annual column changes in (c)CO and (d) HCHO.

1078

1083

1084 Section S6 Impact of Photolysis Changes

1085 The CS2 mechanism featured the updates to photolysis described in section 2. To isolate the impacts of 1086 these changes on tropospheric ozone and OH, a further run was performed using the CS2 mechanism but 1087 with photolysis parameters from the CS mechanism. This run was run for 2 years with the 2nd year 1088 analysed and compared to the same year in the longer CS2 run.

1089

1090The change in photolysis had produced minor changes in tropospheric oxidants. The tropospheric O_3 1091burden decreased by 0.09% (0.32 Tg). Changes in most of the troposphere were below 0.2 ppb (~1%), at1092least an order of magnitude lower than the simulated changes between CS and CS2 (with updated1093photolysis) while larger increases of 0.5-1.5 ppb (0.5-1%) were observed around the tropical tropopause1094(Fig. S27). Therefore, we can conclude the change in O_3 between CS and CS2 s being driven1095predominantly by the change in chemistry rather than photolysis.

1096 1097 Updating the photolysis increased the air mass-weighted OH concentration by 0.98% ($1.0 \times 10^4 \text{ cm}^{-3}$), 1098 compared to a decrease of 1.55% between in CS2 relative to CS. Spatially, OH increased in most of the 1099 troposphere by less than $2.0 \times 10^4 \text{ cm}^{-3}$ (0.2-0.5%) (Fig S28) with the largest absolute increases in at low 1100 altitude 40S-50N. By comparison, OH is simulated to decrease from CS to CS2 in the bulk of the

- 1101 troposphere by at least 2.0×10^4 cm⁻³ and more than 5.0×10^4 cm⁻³ in tropical and midlatitudes (excluding 1102 the tropopause). Therefore, the update to the photolysis, by increasing OH in CS2, actually reduces the
- 1103 change in OH from CS to CS2 rather than being a cause of the mechanistic difference.
- 1104

1105 An important caveat to this is low altitude northern hemisphere midlatitude OH which increased from CS

- to CS2 and also from the base to updated photolysis setup. The impact on OH of the photolysis update
- 1107 must be compared to the impact of the changes to the chemistry, notably isoprene HOx recycling and
- 1108 changes to $O(^{1}D)$'s reaction pathways. Crucially, we see that the change in OH averaged over the lowest
- 1109 500m from CS to CS2 is significantly larger than the change arising from the photolysis update,
- particularly over the regions with significant BVOC emissions such as the Amazon and other tropical regions (Fig. S28). That said, the impact of updated photolysis may be more significant over the parts of
- 1112 Europe and North America where the OH increase between CS and CS2 is smaller. Overall however we
- 1113 can conclude that the update to the photolysis is not a major driver of the significant changes to low
- 1114 altitude OH, rather the update in chemistry between CS and CS2 is the major driver.
- 1115



1116

1118 Figure S22. Zonal mean changes in O₃ (upper panels) and OH (lower panels) between CS2 and

- 1119 CRI_v2_2_photo. The purple line shows the mean tropopause height.
- 1120
- 1121



Figure S23. Change in OH averaged over lowest ~500m between (a) CS2 and CS and (b) CS2 and CRI_v2_2_photo. Note that the scale of (a) is an order of magnitude greater than (b).

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