Supplementary Information for Chapter 4

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B536

B537

B538



B539

B541



Figure S1.1. Flight plans of summer RONOCO flights. For details of each flight, see Table A1 in Appendix A.



B547

B548

B549



B550a and B550b

B552



Figure S1.2. Flight plans of SeptEx flights. For details of each flight, see Table A2 in Appendix A.



Figure S1.3. Flight tracks of winter RONOCO flights. For details of each flight see Table A3 in Appendix A.



Figure S1.4. Flight B534 on 16^{th} July 2010. HO₂ times series (middle panel, black) with altitude (top panel, blue), O₃ (bottom panel, red), and NO₃ (bottom panel, green).



Figure S1.5. Time series as in Figure S1.4, for Flight B535 on 17th July 2010.



Figure S1.6. Time series as in Figure S1.4, for Flight B536 on 19th July 2010.



Figure S1.7. Time series as in Figure S1.4, for Flight B537 on 20th July 2010.



Figure S1.8. Time series as in Figure S1.4, for Flight B538 on 22nd July 2010.



Figure S1.9. Time series as in Figure S1.4, for Flight B539 on 24th July 2010.



Figure S1.10. Flight B541 on 28^{th} July 2010. HO₂ time series (middle panel, black) with altitude (top panel, blue), O₃ (bottom panel, red). NO₃ was not detected during this flight.



Figure S1.11. Flight B545 on 31^{st} August 2010. HO₂ and OH time series (middle panels, black) with altitude (top panel, blue) and O₃ (bottom panel, red).



Figure S1.12. Time series as in Figure S1.11, for flight B546 on 1st September 2010.



Figure S1.13. Time series as in Figure S1.11, for flight B547a on 2nd September 2010.



Figure S1.14. Time series as in Figure S1.11, for flight B547b on 2nd September 2010.



Figure S1.15. Time series as in Figure S1.11, for flight B548 on 3rd September 2010.



Figure S1.16. Time series as in Figure S1.11, for flight B549 on 3rd September 2010.



Figure S1.17. Time series as in Figure S1.11, for flight B550a on 5th September 2010.



Figure S1.18. Time series as in Figure S1.11, for flight B550b on 5th September 2010.



Figure S1.19. Time series as in Figure S1.11 for flight B552 on 9th September 2010.



Figure S1.20. Flight B564 on 11^{th} January 2011. HO₂ time series (middle panel, black) with altitude (top panel, blue), O₃ (bottom panel, red) and NO₃ (bottom panel, green).



Figure S1.21. Time series as in Figure S1.20, for flight B565 on 14th January 2011.



Figure S1.22. Time series as in Figure S1.20, for flight B566 on 16th January 2011.



Figure S1.23. Time series as in Figure S1.20, for flight B567 on 18th January 2011.



Figure S1.24. Time series as in Figure S1.20, for flight B568 on 19th January 2011.



Figure S1.25. Time series as in Figure S1.20, for flight B569 on 20th January 2011.



Figure S1.26. Time series as in Figure S1.20, for flight B570 on 23rd January 2011.



Figure S1.27. Time series as in Figure S1.20, for flight B571 on 24th January 2011.

(a)



HO₂ + CO + OH



 CH_4

18









Figure S1.28. Schemes for reaction of O₃ with a) isobutene; b) *trans*-2-butene; c) *cis*-2-butene; d) 1,3butadiene; e) 1-butene; f) 1-pentene; g) *trans*-2-pentene; h) isoprene. Reaction schemes adapted from the MCM v3.2 (Jenkin *et al.*, 1997, Saunders *et al.*, 2003). The rate constant for decomposition of the Criegee radical is $k_{dec} = 1.0 \times 10^6$ molecule⁻¹ cm³ s⁻¹ (MCM v3.2, Jenkin *et al.*, 1997, Saunders *et al.*, 2003). Channels which are insignificant or unimportant have been shown in grey.



Figure S1.29. Reaction schemes of O_3 -initiated RO₂ radicals which do produce prompt HO₂: a) $C_2H_5O_2$ produced by reactions of O_3 with propene (channel 'b'), *trans*-2-butene, *cis*-2-butene, *trans*-2-pentene (channel 'a'), and isoprene (channel 'a'); b) NC_3H_7O_2 produced by reactions of O₃ with 1-pentene (channel 'b') (see Figure S1.28). Reaction schemes adapted from the MCM v3.2 (Jenkin *et al.*, 1997, Saunders *et al.*, 2003). Channels which are insignificant or unimportant have been shown in grey. The reaction scheme for CH₃O₂ is given in Chapter 4.



Figure S1.30. Reaction schemes for O₃-initiated RO₂ radicals which do not yield prompt HO₂, and are therefore not included in the analysis: a) MVKO₂ produced by O₃ + isoprene, channel 'a' (see Figure S1.28 (g)); b) acyl peroxy radical CH₃C(O)O₂ produced by O₃ + isoprene, channel 'd' (see Figure S1.28 (g): HO₂ is not produced until the third step in the reaction scheme, so this process is considered to be too slow; c) CH₃COCH₂O₂ produced by O₃ + isobutene, channel 'b' (see Figure S1.28 (b)). Reaction schemes adapted from the MCM v3.2 (Jenkin *et al.*, 1997, Saunders *et al.*, 2003).





Figure S1.31. Rates of instantaneous production of HO_2 from reactions of O_3 and NO_3 with alkenes, for RONOCO summer flights. Flight numbers are given in each plot.



Figure S1.32. Rates of instantaneous production of HO_2 from reactions of O_3 with alkenes during SeptEx flights. NO₃ was not detected during SeptEx. Insufficient alkene data were available for flight B547b.





Figure S1.33. Rates of instantaneous production of HO_2 from reactions of O_3 and NO_3 with alkenes during the RONOCO winter flights. Flight numbers are given in each plot.



Figure S1.34. HO₂ versus rates of instantaneous production of HO₂ from reactions of O₃ with alkenes during winter nighttime RONOCO flights. Correlation coefficients (r) are given in each plot. Solid lines are lines of best fit to the data.



Figure S1.35. HO₂ versus rates of instantaneous production of HO₂ from reactions of NO₃ with alkenes during winter nighttime RONOCO flights. Correlation coefficients (r) are given in each plot. Solid black lines are lines of best fit to the data.