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Hohenpeissenberg Photochemical Experiment (HOPE 2000): Measurements and photostationary state calculations of OH and peroxy radicals

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Abstract. Measurements of OH, total peroxy radicals, non-methane hydrocarbons (NMHCs) and various other trace gases were made at the Meteorological Observatory Hohenpeissenberg in June 2000. The data from an intensive measurement period characterised by high solar insolation (18-21 June) are analysed. The maximum midday OH concentration ranged between 4.5x10^{6} molecules cm^{-3} and 7.4x10^{6} molecules cm^{-3}. The maximum total RO_x (RO_x =OH+RO+HO_2+RO_2) mixing ratio increased from about 55 pptv on 18 June to nearly 70 pptv on 20 and 21 June. A total of 64 NMHCs, including isoprene and monoterpenes, were measured every 1 to 6 hours. The oxidation rate of the NMHCs by OH was calculated and reached a total of over 14x10^{6} molecules cm^{-3} s^{-1} on two days. A simple photostationary state balance model was used to simulate the ambient OH and peroxy radical concentrations with the measured data as input. This approach was able to reproduce the main features of the diurnal profiles of both OH and peroxy radicals. The balance equations were used to test the effect of the assumptions made in this model. The results proved to be most sensitive to assumptions about the impact of unmeasured volatile organic compounds (VOC), e.g. formaldehyde (HCHO), and about the partitioning between HO_2 and RO_2. The measured OH concentration and peroxy radical mixing ratios were reproduced well by assuming the presence of 3 ppbv HCHO as a proxy for oxygenated hydrocarbons, and a HO_2/ RO_2 ratio between 1:1 and 1:2. The most important source of OH, and conversely the greatest sink for peroxy radicals, was the recycling of HO_2 radicals to OH. This reaction was responsible for the recycling of more than 45x10^{6} molecules cm^{-3} s^{-1} on two days. The most important sink for OH, and the largest source of peroxy radicals, was the oxidation of NMHCs, in particular, of isoprene and the monoterpenes.

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