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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observation and modelling of OH and HO₂ concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere" *by* K. D. Lu et al.

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In Fig. 3 of our paper, we compare measured and modelled relative detection sensitivities (α_{RO_2}) for specific RO_2 that are detected by our LIF system in the HO_2 cell. As noted in the text (Sect. 2.3), the modelled α_{RO_2} values (blue symbols, MCMv3.1) reproduce the pattern of the experimental values relatively well. However, some underprediction is evident for particular peroxy radicals, e.g. of cyclohexane, MACR and MVK. After paper submission, we have recalculated the α_{RO_2} values using the newly published Master Chemical Mechanism MCMv3.2 (http://mcm.leeds.ac.uk/MCM/home.htt). In-

terestingly (and as one would hope), the new MCM version yields generally improved agreement between the simulated and experimental α_{RO_2} values (see Fig. 1, below). More specifically, for peroxy radicals from isoprene, MACR and cyclohexane, α_{RO_2} is much better described by MCMv3.2 rather than by MCMv3.1. Thus, the measurements by Fuchs et al. (2011) give indirect support to the revisions made for these species in MCMv3.2. It should be noted that the modelled target parameter, α_{RO_2}, is related to a short time scale (2.7 ms), high NO mixing ratio (1500 ppm), low pressure (3.5 hPa) and dark conditions, quantifying the RO_2 to HO_2 conversion at chemical conditions where peroxy radicals preferentially react with NO.

The improved model results for the peroxy radicals from isoprene, MACR and cyclohexane are caused by enhanced HO_2 formation.

Isoprene: the HO_2 yield from the unimolecular decomposition reaction of ISOPBO radicals (β-hydroxyalkoxy radicals from 1,2 OH addition) is enhanced due to replacement of reaction **R1** (MCMv3.1) by reaction **R2** (MCMv3.2).

R1: ISOPBO $\rightarrow 0.75 \times (\mathrm{MVK} + \mathrm{HCHO} + \mathrm{HO_2}) + 0.25 \times (\mathrm{MVKOH} + \mathrm{CH_3O_2})$
R2: ISOPBO $\rightarrow \mathrm{MVK} + \mathrm{HCHO} + \mathrm{HO_2}$

MACR: the yield of β-hydroxyperoxy radicals (MACRO2, MACROHO2), which undergo fast decomposition to HO_2, is enhanced due to replacement of reaction **R3** (MCMv3.1) by reaction **R4** (MCMv3.2). The yield of MACO3, which does not contribute to the interference, is diminished.

R3: MACR + OH $\rightarrow 0.57 \times$ MACO3 $+ 0.43 \times$ MACRO2
R4: MACR + OH $\rightarrow 0.45 \times$ MACO3 $+ 0.47 \times$ MACRO2 $+ 0.08 \times$ MACROHO2

Cyclohexane: α_{RO_2} is strongly enhanced by the newly included ring-opening reaction pathway for the cyclohexoxy radical in MCMv3.2. In the ring-opening mechanism (missing in MCMv3.1), the major product CO1C6O undergoes 1,5 H-atom shift and isomerization to δ-hydroxylalkoxy radicals (CO1H63O). The latter product decomposes to

HO_2 as fast as β-hydroxylalkoxy radicals.

Figure 1 Relative detection sensitivities ($\alpha^{i}_{RO_2}$) for specific RO_2 compared to HO_2. The experimental values (red stars) and their 1σ error bars were determined for the instrument configuration applied at PRD for HO_2 detection (Fuchs et al., 2011). Modelled values (blue circles for MCMv3.1 and green crosses for MCMv3.2) are shown for major VOCs which contributed more than 90 % to the VOC reactivity in PRD. Original and mechanistic names of the VOCs are shown at the lower and upper x-axis, respectively.

Reference Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and Wahner, A.: Detection of HO_2 by laser-induced fluorescence: calibration and interferences from RO_2 radicals, Atmos. Meas. Tech. Discuss., 4, 1255–1302, doi10.5194/amtd-4-1255-2011, 2011.

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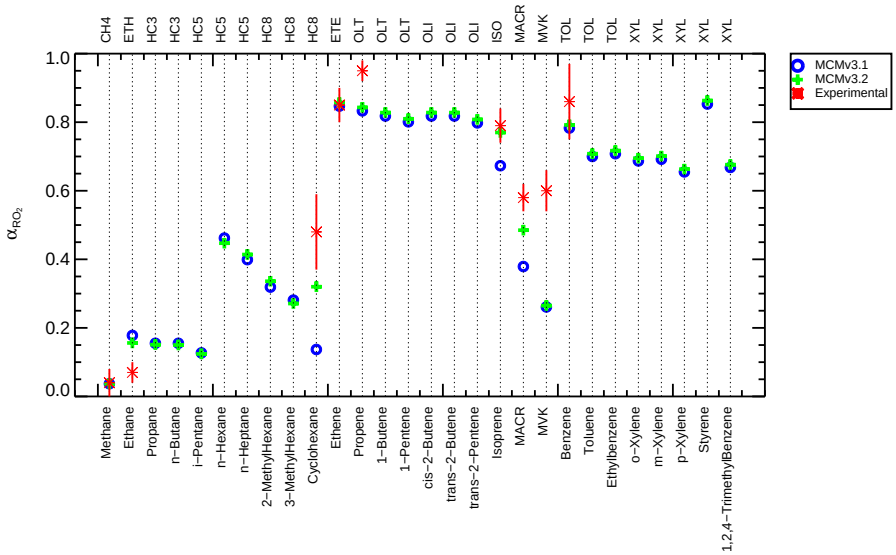

Fig. 1. This updated figure is planned to replace Fig. 3 of the manuscript