

Product Study of the Reaction of OH Radicals with DMS under low-NO_x conditions



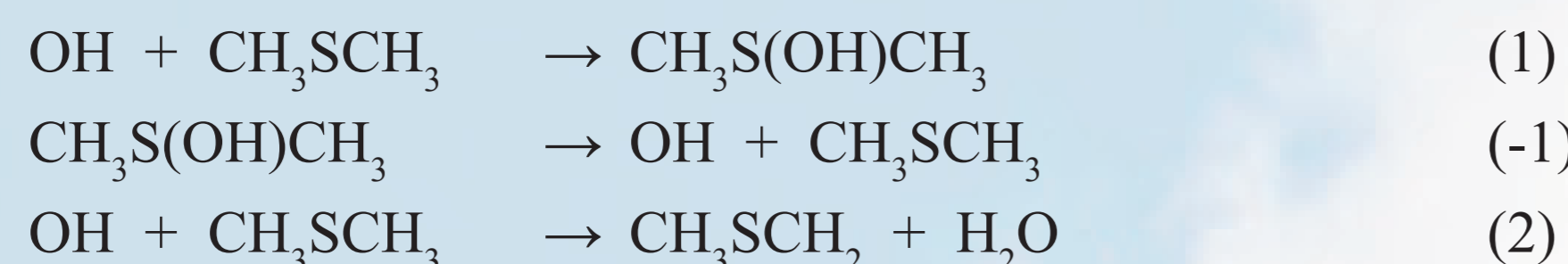
LEIBNIZ INSTITUTE FOR TROPOSPHERIC RESEARCH

T. Berndt and S. Richters
Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, D-04318 Leipzig, Germany
berndt@tropos.de

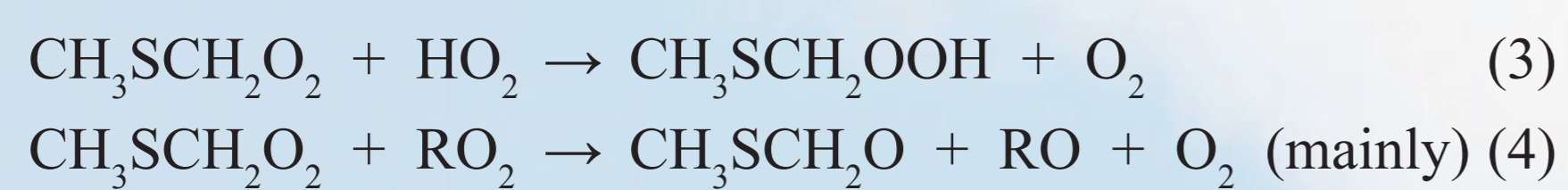
Introduction

Dimethylsulfide (DMS; CH₃SCH₃) is produced by biological activity of phytoplankton in the ocean's surface. DMS represents the largest natural source of atmospheric sulphur accounting for approximately 60% of biogenic emissions (Bates et al., 1992, Spiro et al., 1992). The atmospheric degradation of DMS is nearly exclusively initiated by the attack of OH radicals producing among others SO₂ and subsequently sulphuric acid aerosols. According to the CLAW hypothesis the aerosol formation could play an important role for the radiation budget and possibly for climate regulation (Charlson et al., 1987). Up to now there are a limited number of laboratory studies investigating product formation from the atmospheric reaction of OH radicals with DMS under low-NO_x conditions relevant for the remote maritime environment (Barnes et al., 1988, Arsene et al., 1999). The degradation processes, including SO₂ formation, are not fully understood so far. An overview of the current state of knowledge regarding atmospheric DMS conversion is given by Barnes et al. (2006). A corresponding modelling module is available from the Master Chemical Mechanism, MCMv3.2.

The primary attack of OH radicals toward DMS proceeds via a reversible addition channel, path (1)/(-1), competing with a H-abstraction channel, path (2).



The OH-DMS adduct (CH₃S(OH)CH₃) reacts further with O₂ by H-abstraction forming dimethyl sulfoxide (DMSO) or probably by O₂ addition with subsequent formation of dimethyl sulfone (DMSO₂). Consecutive reaction of the CH₃SCH₂ radical with O₂ yields the corresponding peroxy radical (CH₃SCH₂O₂) that in the absence of NO_x reacts either with HO₂ or in a self- or cross reaction with other peroxy radicals.



CH₃SCH₂O undergoes rapid decomposition in a time scale of microseconds forming CH₃S and HCHO (Urbanski et al., 1997).



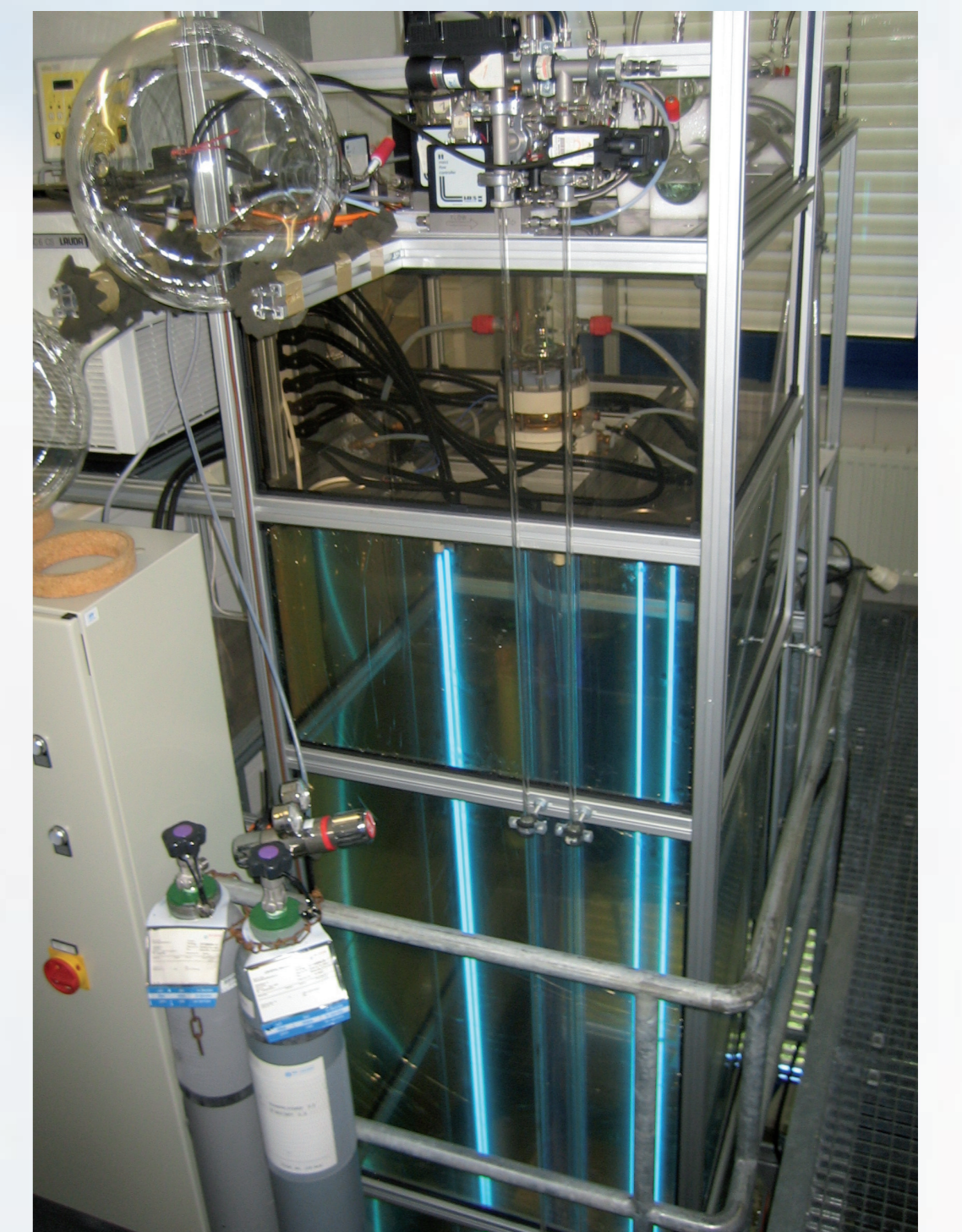
The atmospheric fate of CH₃S is key step for the formation of SO₂ and subsequently H₂SO₄ as well as for the MSA production.

Subject of the present study is the formation of first stable products from the reaction of OH radicals with DMS under low NO_x conditions. A comparison with modelling results using a state-of-the-art mechanism module (MCMv3.2) should reveal how accurate modelling is able to describe the DMS degradation process at the moment.

Experimental setup

- atmospheric pressure flow-tube IFT-LFT (i.d. 8 cm; length 505 cm; 8 UV Hg-lamps with a cut-off wavelength of 210 nm)
- T = 293 ± 0.5 K; carrier gas: synthetic air or N₂/O₂ mixture
- total flow rate of 10 dm³ min⁻¹ (STP) resulting in a bulk residence time in the irradiated section of 97 sec
- NO and NO₂ background concentrations of about 10¹⁰ molecule cm⁻³ or below
- OH radical formation: H₂O₂ photolysis under dry conditions or O₃ photolysis at a relative humidity of 50 %
- H₂O₂ from saturator (30% H₂O₂ solution); O₃ from ozone generator UVP OG-2
- O₃, SO₂ and NO_x measured by gas monitors
- FT-IR spectroscopy (path length: 20 m, Nicolet 6700, MCT detector) for the detection of H₂O₂ and HCHO
- proton transfer reaction mass spectrometry (Ionicon PTR-MS HS) measuring the disappearance of DMS and product formation

Modelling: The reaction mechanism used for the modelling studies was taken from the Master Chemical Mechanism, MCMv3.2. In contrast to the original mechanism, CH₃SCHO formation via CH₃SCH₂O₂ + HO₂ was omitted.



Product formation in dependence on O₂

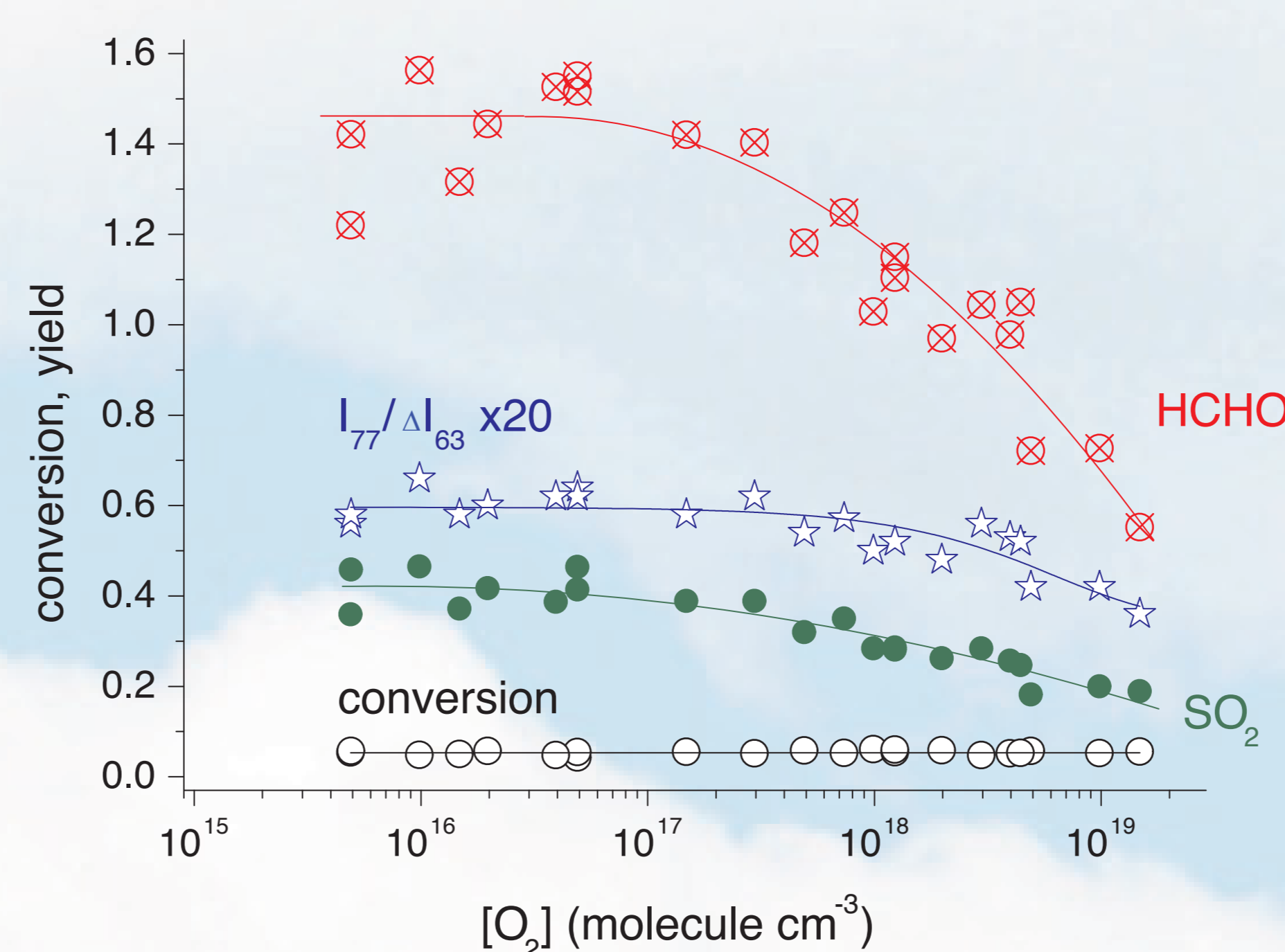


Figure 3: DMS conversion and the formation yields of HCHO, SO₂ and the signal ratio I₇₇/ΔI₆₃ (stands for CH₃SCHO yield) as a function of O₂ concentration. OH radical formation via H₂O₂ photolysis. Initial concentrations (in molecule cm⁻³): [H₂O₂] = 2.0 · 10¹³; [DMS] = 1.35 · 10¹³.

According to the O₂-dependent branching ratio of H-abstraction vs. addition channel the product yields show a clear O₂ dependence. For [O₂] < 10¹⁷ molecule cm⁻³, H-abstraction is practically the only process. At atmospheric conditions the addition channel accounts for about 30 % of DMS conversion. The results suggest that HCHO, SO₂ and CH₃SCHO are representing products mainly from H-abstraction.

PTR-MS Measurements

Product spectra by normal DMS and DMS-d₆

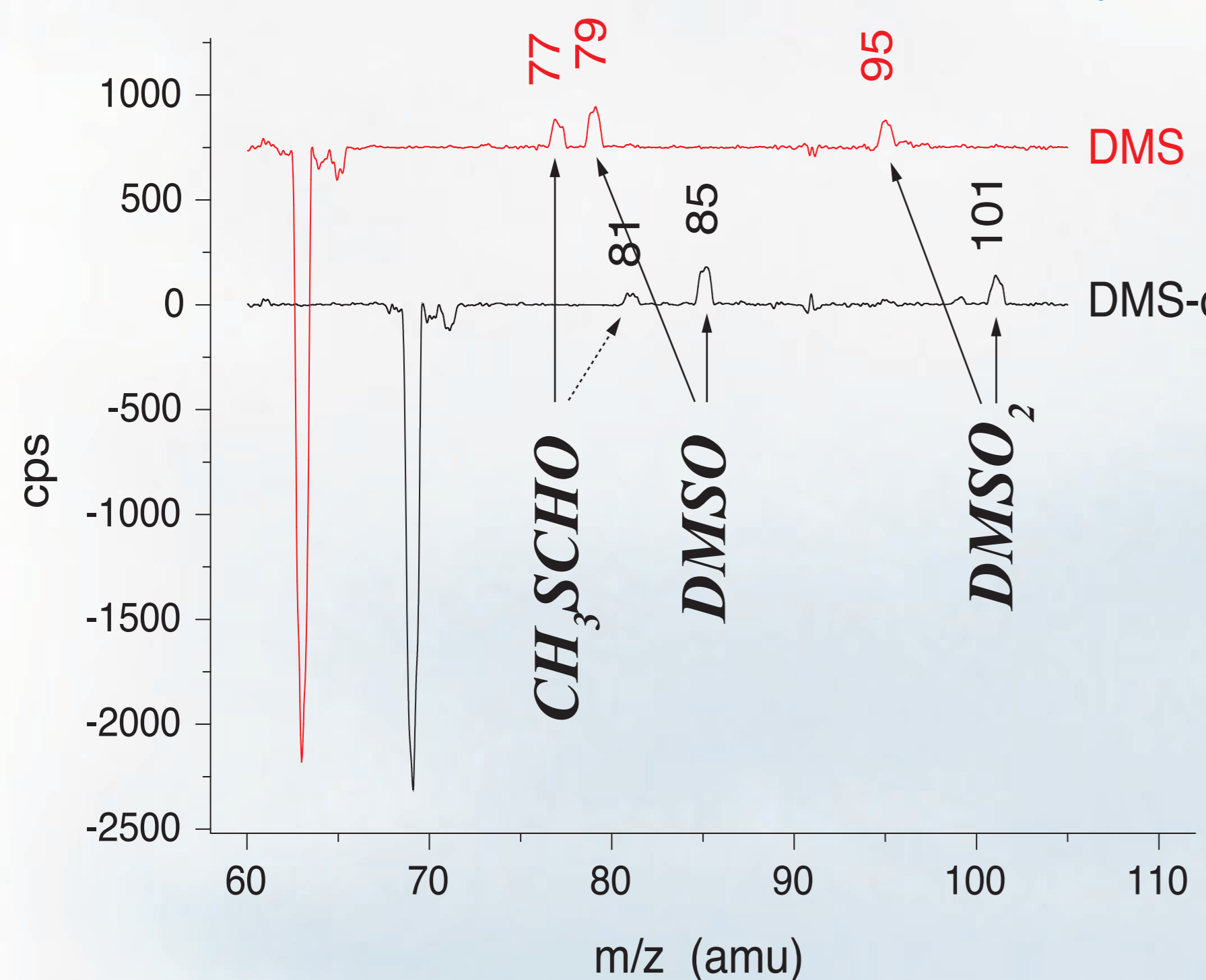


Figure 1: Difference mass spectra (OH formation on/off) from the reaction of OH radicals with DMS or DMS-d₆. Consumed reactants appear as negative signals. OH radical generation via O₃ photolysis at r.h. = 50 %. Initial concentrations: [O₃] = 2.17 · 10¹² molecule cm⁻³, [DMS] or [DMS-d₆] = 1.5 · 10¹² molecule cm⁻³.

Typical PTR-MS experiment

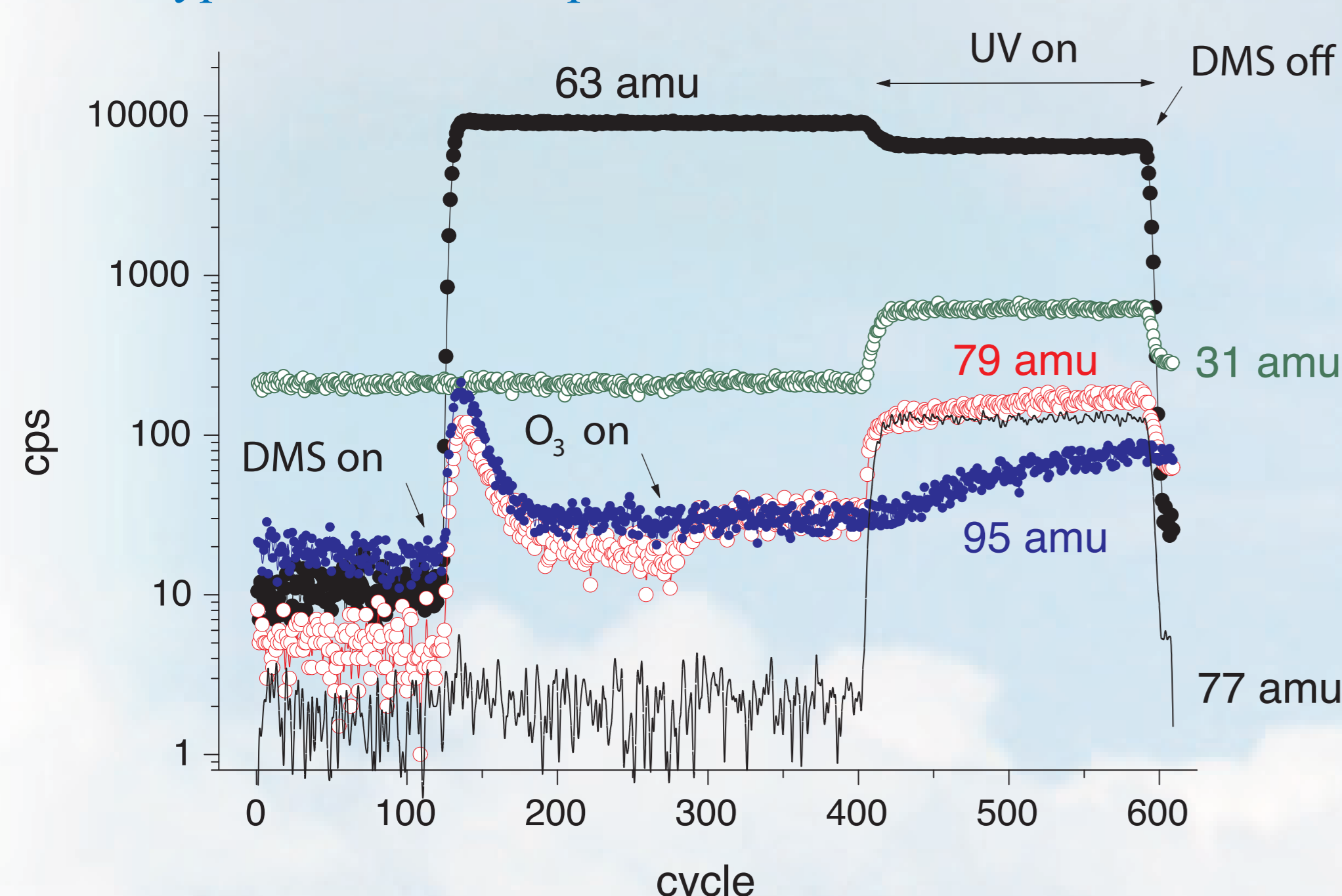


Figure 2: Typical progress of a measurement by means of PTR-MS detection. The ion traces stand for the protonated ions of: HCHO (31 amu), DMS (63 amu), CH₃SCHO (77 amu), DMSO (79 amu), DMSO₂ (95 amu)

Influence of [DMS] / [H₂O₂]

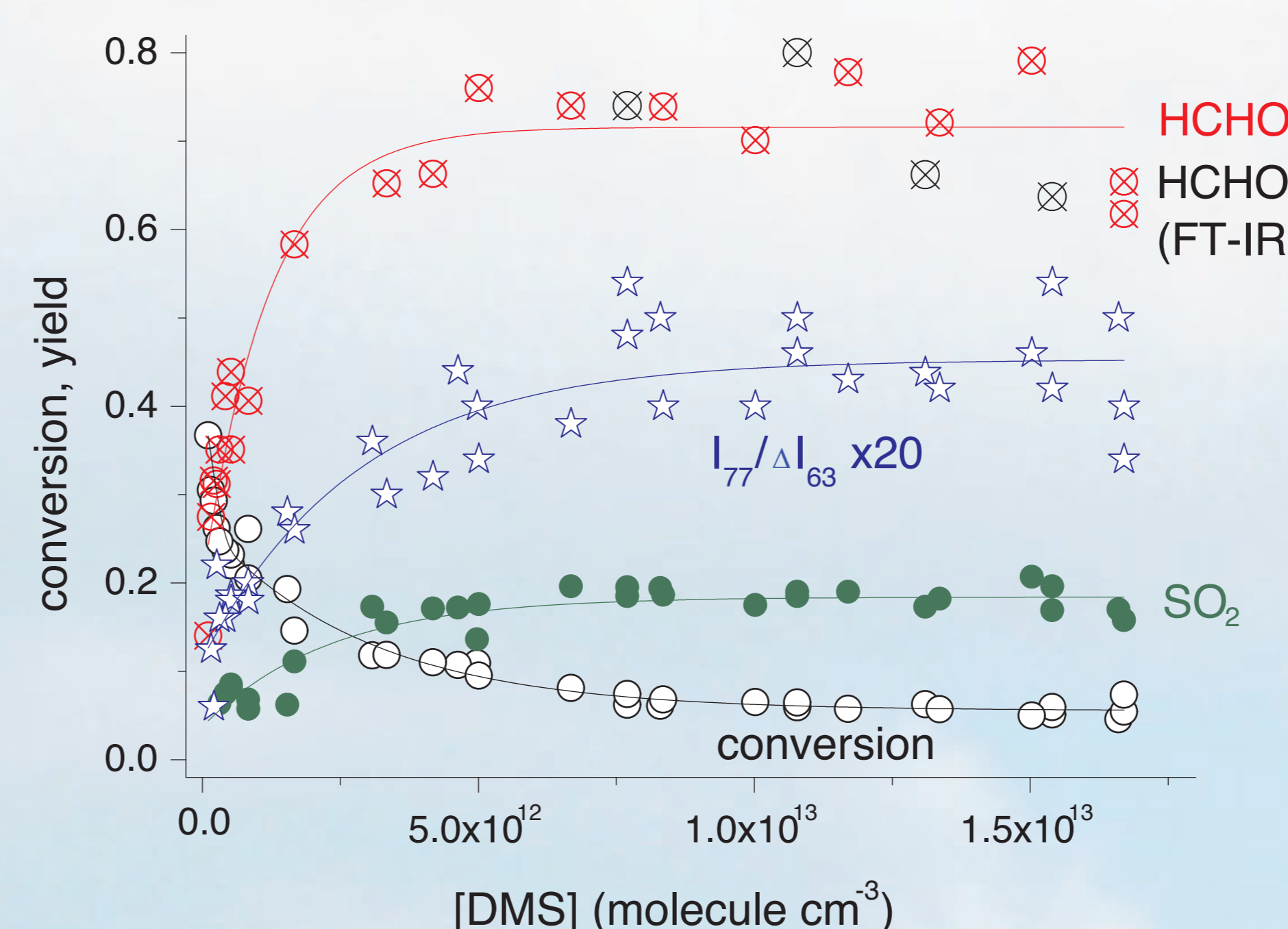


Figure 4: Product formation and DMS conversion as a function of DMS concentration for nearly constant H₂O₂ concentration, i.e. constant OH formation rate, [H₂O₂] ~ 1.5 · 10¹³ molecule cm⁻³.

With lowering of the DMS concentration (constant OH formation rate) HO₂ formation via OH + H₂O₂ → HO₂ + H₂O becomes more important favouring the reaction of CH₃SCH₂O₂ with HO₂ in competition with the self- and cross reaction with RO₂. HCHO, SO₂ and CH₃SCHO are final products from CH₃SCH₂O₂ self- and cross reactions.

Importance of O₃

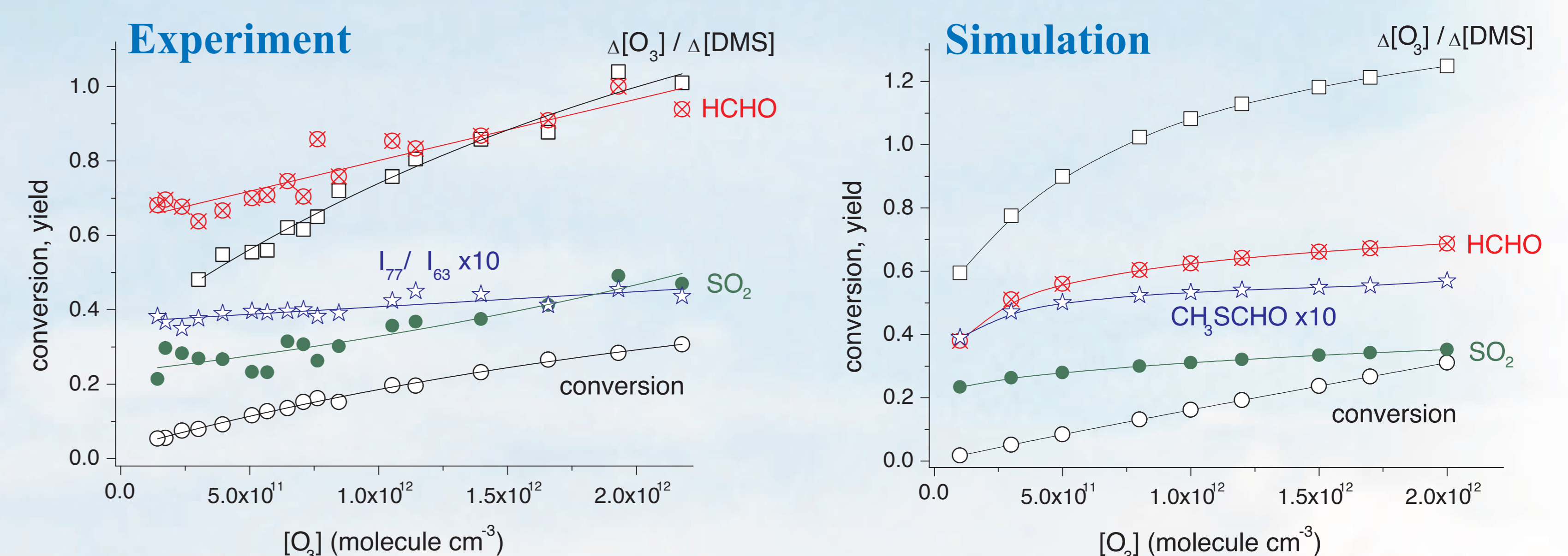


Figure 5: Influence of O₃ concentration on product formation; O₃ photolysis at r.h. = 50 %; [DMS] = 1.5 · 10¹² molecule cm⁻³. For [O₃] ≤ 5 · 10¹¹ molecule cm⁻³ there is no clear influence of O₃ on product yields. Modelling clearly underestimated HCHO formation, apart from that MCMv3.2 represents a useful tool for the modelling of the OH + DMS reaction.

References:

- Arsene, C., Barnes, I., Becker, K.-H., PCCP, 1999, **1**, 5463-5470.
- Barnes, I., Bastian, V., Becker, K.-H., Int. J. Chem. Kinet., 1988, **20**, 415-431.
- Barnes, I., Hjorth, J., Mihalopoulos, N., Chem. Rev., 2006, **106**, 940-975.
- Bates, T.S., Lamb, B.K., Guenther, A., Dignon, J., Stoiber, R.E., J. Atmos. Chem., 1992, **14**, 315-337.
- Charlson, R.J., Lovelock, J.E., Andreae, M.O., Warren, S.G., Nature, 1987, **326**, 655-661.
- Spiro, P.A., Jacob, D.J., Logan, J.A., J. Geophys. Res., 1992, **97(D5)**, 6023-6036.
- Urbanski, S.P., Stickel, R.E., Zhao, Z., Wine, P.H., J. Chem. Soc. Faraday Trans., 1997, **93(16)**, 2813-2819.

Acknowledgement:

The authors thank K. Pielok and A. Rohmer for technical support.