

Product Study of the Reaction of OH Radicals with Isoprene



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Introduction

Isoprene (2-methyl-1,3-butadiene) represents the dominant non-methane hydrocarbon emitted into the atmosphere by vegetation with a global emission rate of $\sim 5 \cdot 10^8$ tons per year. Atmospheric mixing ratios for isoprene span a range of 0.3 - 10 ppb [1]. The degradation process is governed by the initial attack of OH radicals at daytime resulting in a lifetime of ~ 1.5 h [2]. Chemical processes going on in the course of isoprene transformation and formed products are important issues in atmospheric chemistry. At the present time, new experimental findings from field and laboratory investigations [3,4] as well as results from quantum-chemical calculations [5] are discussed intensively in the literature reactivating experimental effort in the lab for validation of new product channels for the atmospheric reaction of OH radicals with isoprene as proposed recently.

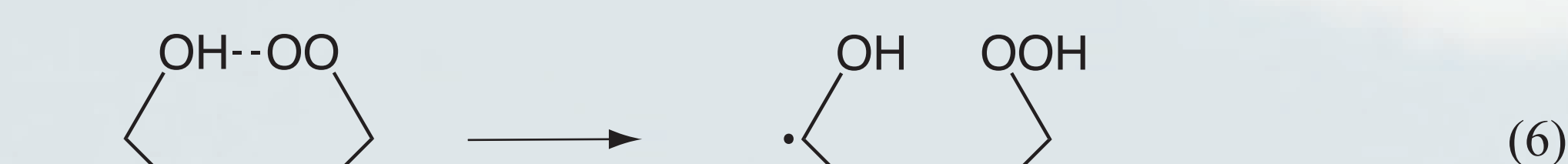
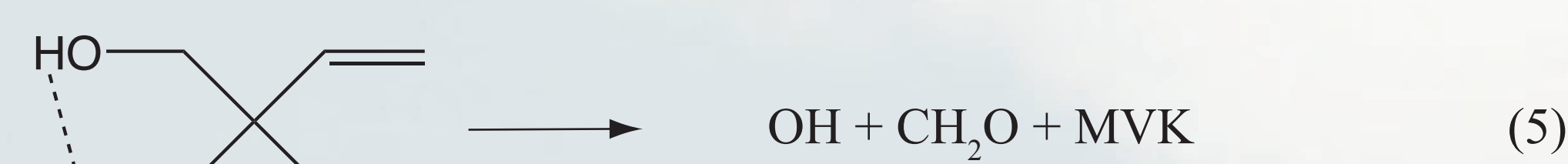
The OH attack towards isoprene (C_5H_8) proceeds predominantly at terminal positions (terminal: 90%, inner: 10%) resulting in the presence of O_2 in six different hydroxy-peroxy radicals ($HO-C_5H_8-O_2$) with *cis*- and *trans*-isomers.



The fate of $HO-C_5H_8-O_2$ is governed by the reaction with HO_2 , NO , RO_2 or by rearrangement (with subsequent decomposition) in dependence on the availability of the reactants.



E.g. for rearrangement the 1,2 adduct (1,5-H shift) and the *cis*-1,4 adduct (1,6-H shift) [5].



Reaction scheme applied for modelling (main tube)

| path | k ($\text{cm}^3 \text{ s}^{-1}$ or s^{-1}) |
|---|---|
| $NO + HO_2 \longrightarrow OH + NO_2$ | $8.9 \cdot 10^{-12}$ |
| $OH + HO_2 \longrightarrow H_2O + O_2$ | $1.1 \cdot 10^{-10}$ |
| $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$ | $3.0 \cdot 10^{-13}$ |
| $OH + C_5H_8(O_2) \longrightarrow RO_2$ | $1.0 \cdot 10^{-10}$ |
| $RO_2 + HO_2 \longrightarrow ROOH + O_2$ | $1.7 \cdot 10^{-11}$ |
| $RO_2 + NO \longrightarrow \text{carbonyl} + HO_2 + NO_2$ | $8.9 \cdot 10^{-12}$ |
| $RO_2 + RO_2 \longrightarrow 1.6 \text{ carbonyl} + 1.6 HO_2$ | $5.0 \cdot 10^{-12}$ |
| RO_2 | 0.36 |

Moderate HO_2

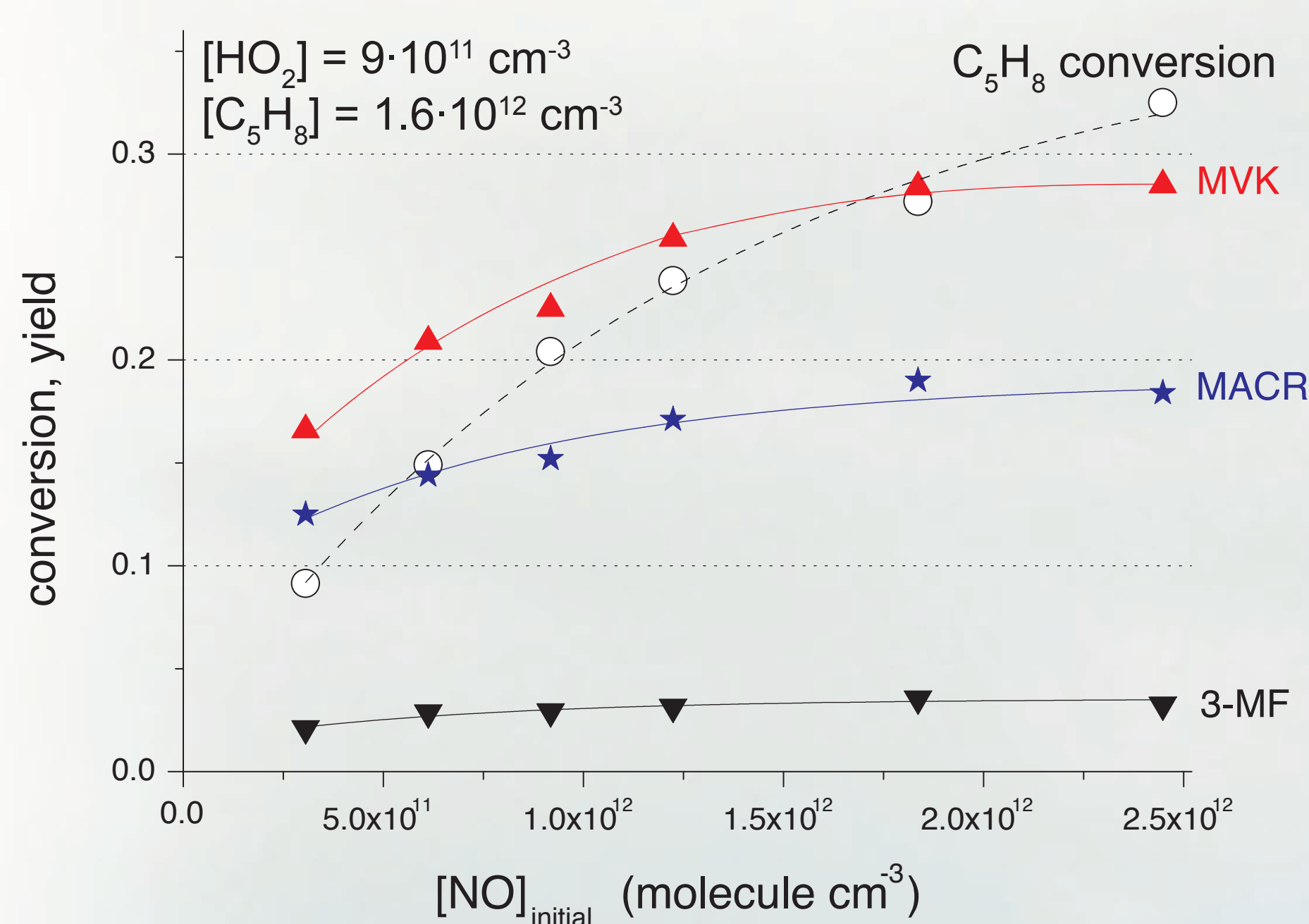


Figure 1a: Measured C_5H_8 conversion as well as formation yields of methyl-vinyl-ketone (MVK), methacrolein (MACR) and 3-methyl furan (3-MF) as a function of added NO. 3-MF yield increases from 2.1% to 3.3% with increasing NO. For highest NO, 28.5% MVK and 18.5% MACR are detected

Modelling results

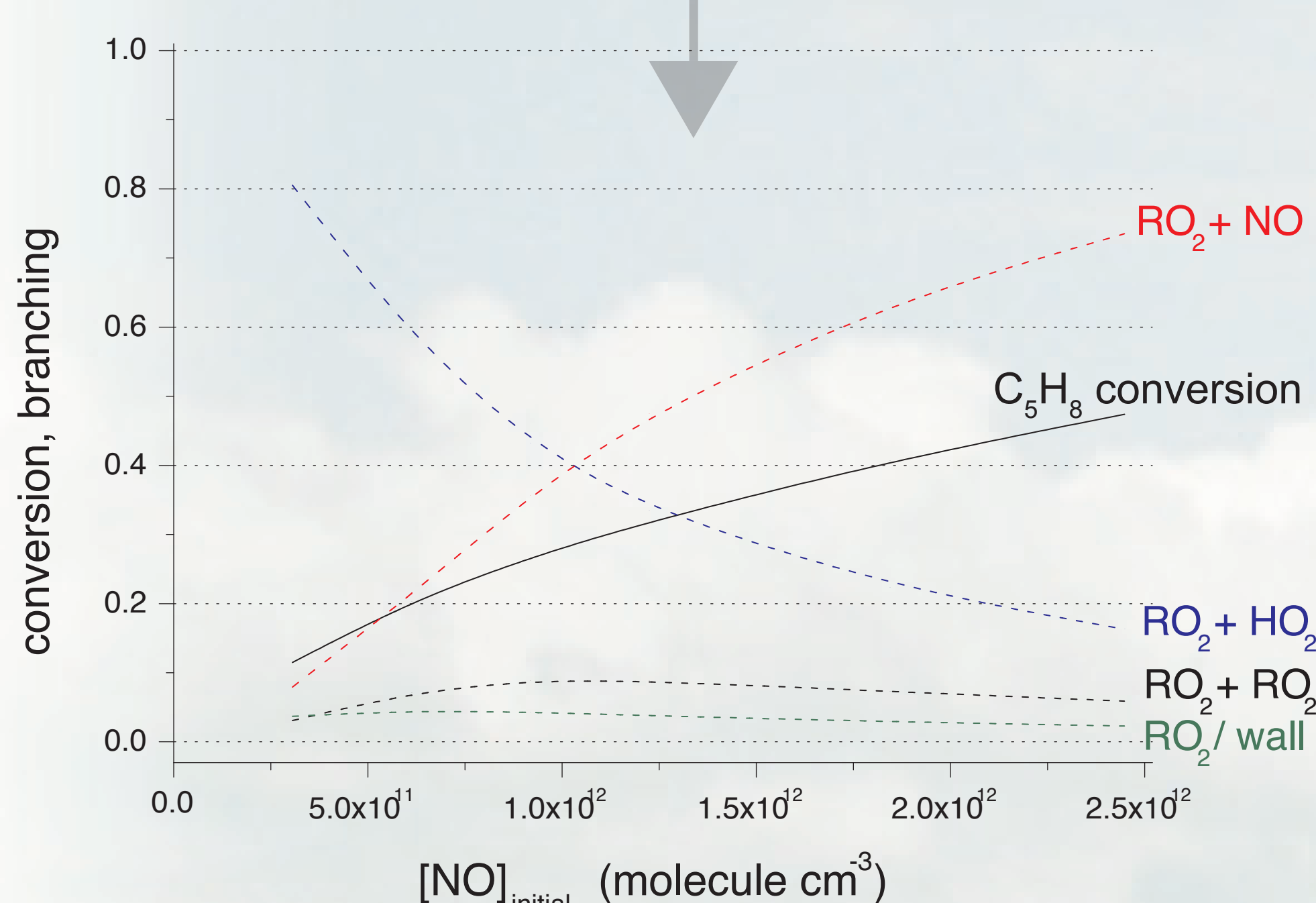


Figure 1b: Modelling suggests that for lowest NO the fate of RO_2 is governed by the reaction with HO_2 (ca.80%) with measured yields of 17% MVK and 12% MACR. For highest NO, RO_2 react mainly with NO (ca.75%). Extrapolation to a total reaction of RO_2 by NO points to about 30% MVK and 20% MACR being in good agreement with former studies. The cross reaction of RO_2 , as well as wall loss are of less important.

References:

- [1] C. Wiedinmyer, et al., Atmos. Environ., 35 (2001) 1001.
- [2] H. X. Chen, D. Hulbert, P. B. Shepson, J. Geophys. Res., 103 (1998) 25563.
- [3] J. Lelieveld, et al., Nature, 452, (2008) 737.
- [4] F. Paulot, et al., Science, 325 (2009) 730.
- [5] J. Peeters, T. L. Nguyen, L. Vereecken, Phys. Chem. Chem. Phys., 11 (2009) 5935.
- [6] A. Miyoshi, et al., J. Geophys. Res., 99 (1994) 18779.

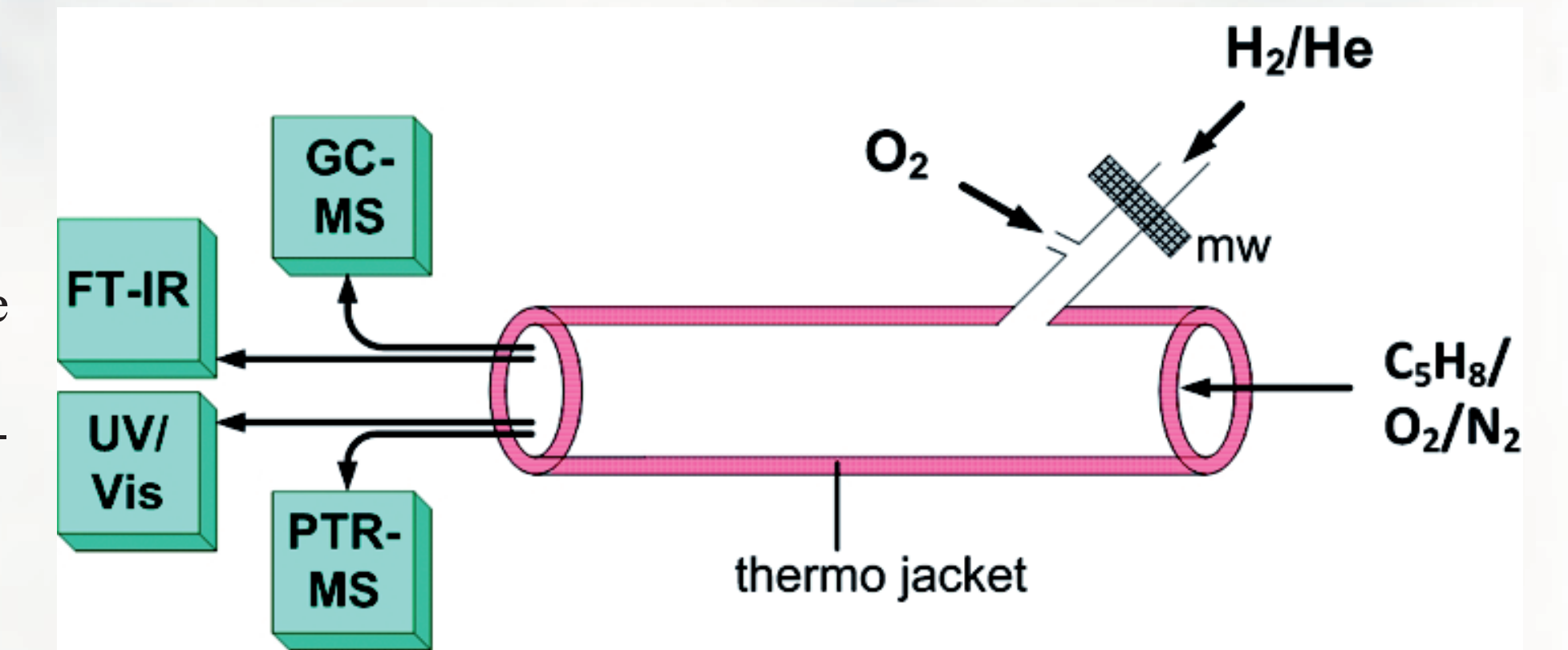
Experimental setup

The reaction of OH radicals with isoprene was conducted in a flow tube at 295 ± 2 K and a total pressure of 0.25 bar. OH radicals are formed via the reaction sequence $H + O_2 + M \rightarrow HO_2 + M$ (side arm) and $NO + HO_2 \rightarrow OH + NO_2$ (main tube). Analysis of reaction products has been performed by means of i) CI-MS (Ionicon) using H_3O^+ as the reagent ion, ii) on-line coupled GC-MS (Agilent) with cryo-enrichment, iii) long-path FT-IR spectroscopy (path length: 20 m, Nicolet), and iv) long-path UV spectroscopy (path length: 422 cm, PerkinElmer).

Side arm:

- inner diameter: 7 mm, quartz
- 0.05% H_2 in He
- chilled mw cavity, gas temperature controlled at the entrance to the main tube
- residence time downstream O_2 addition before entering main tube: 20 ms
- $[O_2] = 1.2 \cdot 10^{18}$ molecule cm^{-3}
- complete conversion of H-atoms to HO_2

Main tube (inner diameter: 40 mm; length: 50 cm): The total gas flow was set at 10 litre/min STP resulting in a bulk residence time of 0.87 sec. Initial HO_2 concentration was determined by adding an excess of NO_2 instead of C_5H_8 ($[NO_2] = (2.3 - 4.6) \cdot 10^{14}$ molecule cm^{-3}) and measuring produced HO_2NO_2 by means of FT-IR spectroscopy. NO premixed with the carrier gas was added to the main stream together with C_5H_8 . The O_2 concentration in the main tube was $1.2 \cdot 10^{18}$ molecule cm^{-3} .



Excess of HO_2

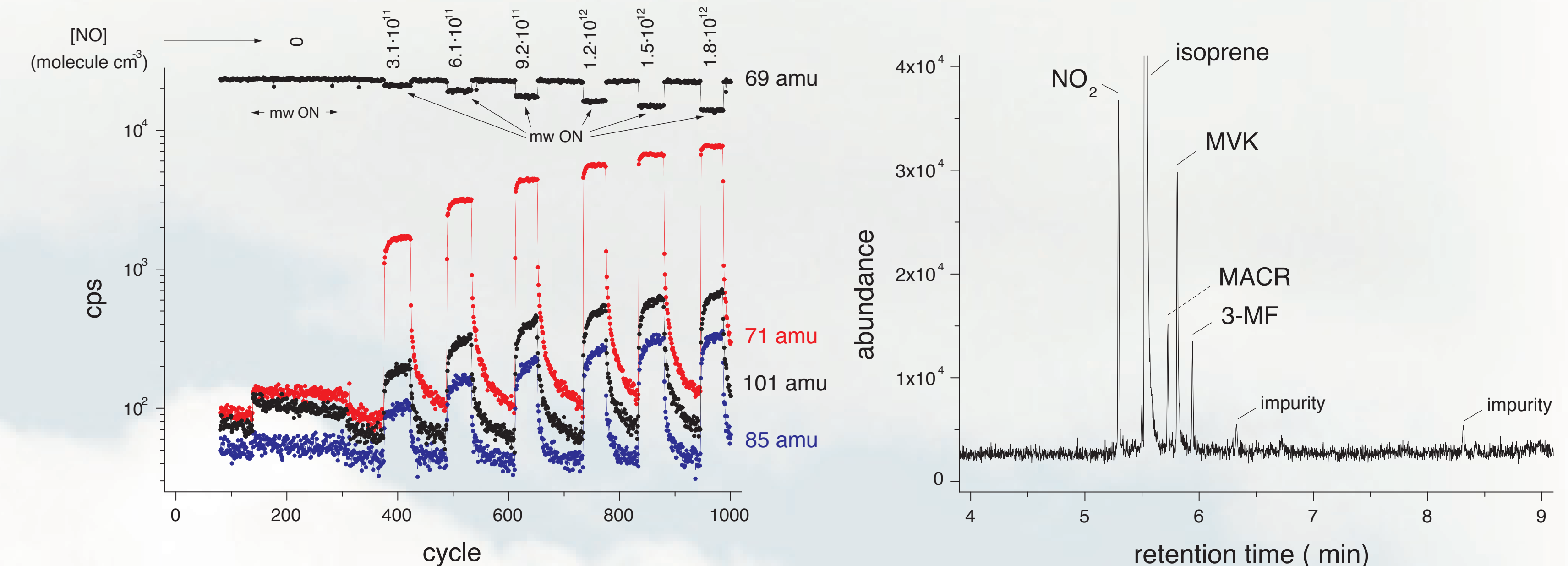


Figure 2: PTR-MS analysis: Ion traces at 69, 71, 85, and 101 amu for different reaction conditions, microwave discharge (mw) ON/OFF for different NO concentrations, see also Fig.4a. 69 amu stands for $C_5H_8-H^+$, 71 amu for $MVK-H^+$ and $MACR-H^+$ in total, 85 amu probably for $C_5H_8O-H^+$, and 101 amu probably for $HO-C_5H_8-OOH-H^+$ - 18 amu (H_2O splitting-off).

Figure 3: GC-MS analysis: Total ion chromatogram (45-120 amu) of the experiment using $[NO] = 6.1 \cdot 10^{11}$ molecule cm^{-3} , see also Fig.2 and Fig.4a. Measured product concentrations are (unit: molecule cm^{-3}): MVK: $4.2 \cdot 10^{10}$, MACR: $2.9 \cdot 10^{10}$, 3-MF: $5.9 \cdot 10^9$.

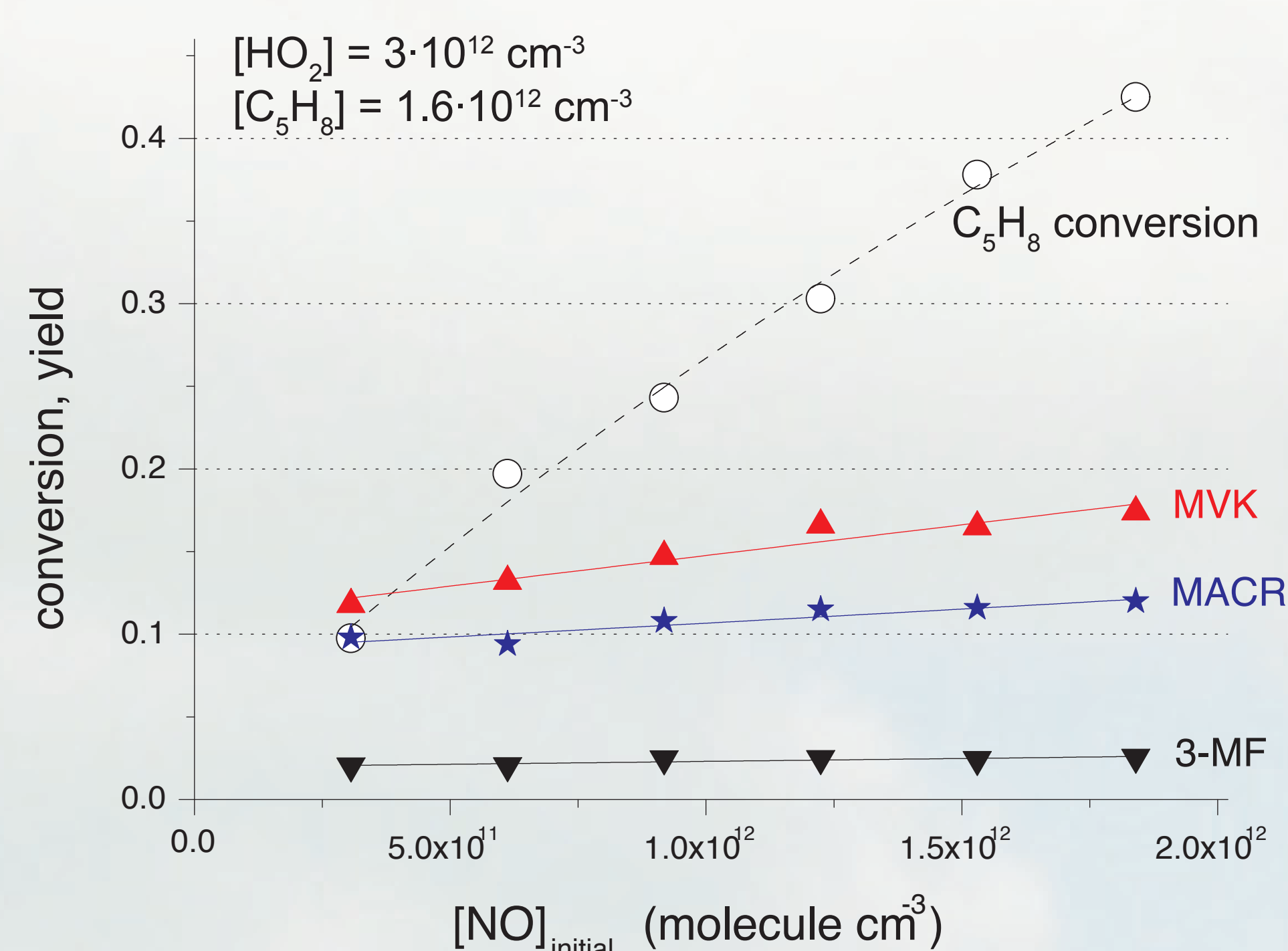


Figure 4a: C_5H_8 conversion and the formation yields of methyl-vinyl-ketone (MVK), methacrolein (MACR) and 3-methyl furan (3-MF) obtained for different NO concentrations. With increasing NO the products yields increase from 12% to 17% (MVK), from 10% to 12% (MACR), and from 2.0% to 2.6% (3-MF). The NO_2 yield with respect to initial NO is in each case $> 95\%$ (FT-IR analysis).

Modelling results

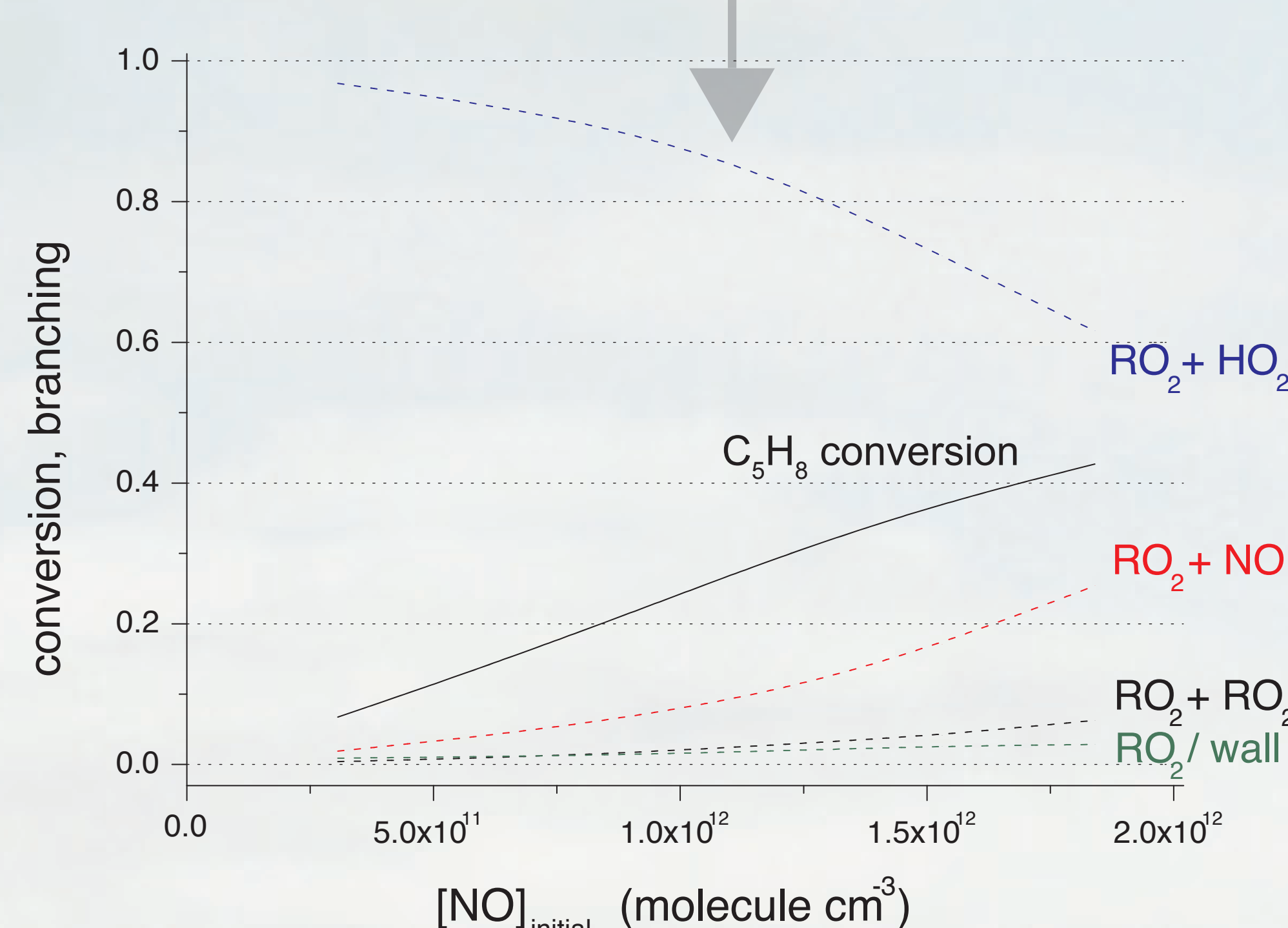


Figure 4b: Modelling results indicate a preferred reaction of RO_2 with HO_2 (97%) for the lowest NO concentration used. For highest NO about 62% of RO_2 reacted with HO_2 and 25% with NO. Modelling describes well C_5H_8 conversion. A sensitivity study showed that uncertainties for $k(RO_2+RO_2)$ do not basically influence the output of modelling.

Summary and Conclusion

- for nearly exclusive reaction of RO_2 with HO_2 about 20% MVK and MACR in total are measured as well as 2% 3-MF and an unidentified species (C_5H_8O)
- hydroxy-hydroperoxides are not the only products of $RO_2 + HO_2$
- Paulot et al. [4] indicated a 12% channel forming OH and carbonyls
- Miyoshi et al. [6] reported negligible carbonyl formation by $RO_2 + HO_2$