

# Influence of Biogenic VOCs on Photooxidant Formation: Simulation Experiments in EUPHORE and Comparison with Model Calculations

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## Introduction

The possible contribution of biogenic VOCs to tropospheric ozone formation even in highly developed regions like central Europe or the eastern United States is strongly discussed. Isoprene and monoterpenes account for a main fraction of the biogenic VOC emissions. Several recent field studies have shown situations where isoprene in fact dominates the daytime photochemistry and thereby contributes strongly to the regional ozone formation (Staffelbach *et al.*, 1997; Biesenthal *et al.*, 1998; Roberts *et al.*, 1998). Despite recent progress, the degradation mechanisms of monoterpenes are far from being sufficiently understood and even in the case of isoprene the quantified products account for only 60 - 70% of the carbon balance. Due to the complexity of the compounds and their reactions, causing exceptional analytical difficulties, this knowledge is likely to improve only gradually.

This work represents a complementary, not alternative, integrated approach to the investigation of mechanistic details in laboratory studies.

## Experimental

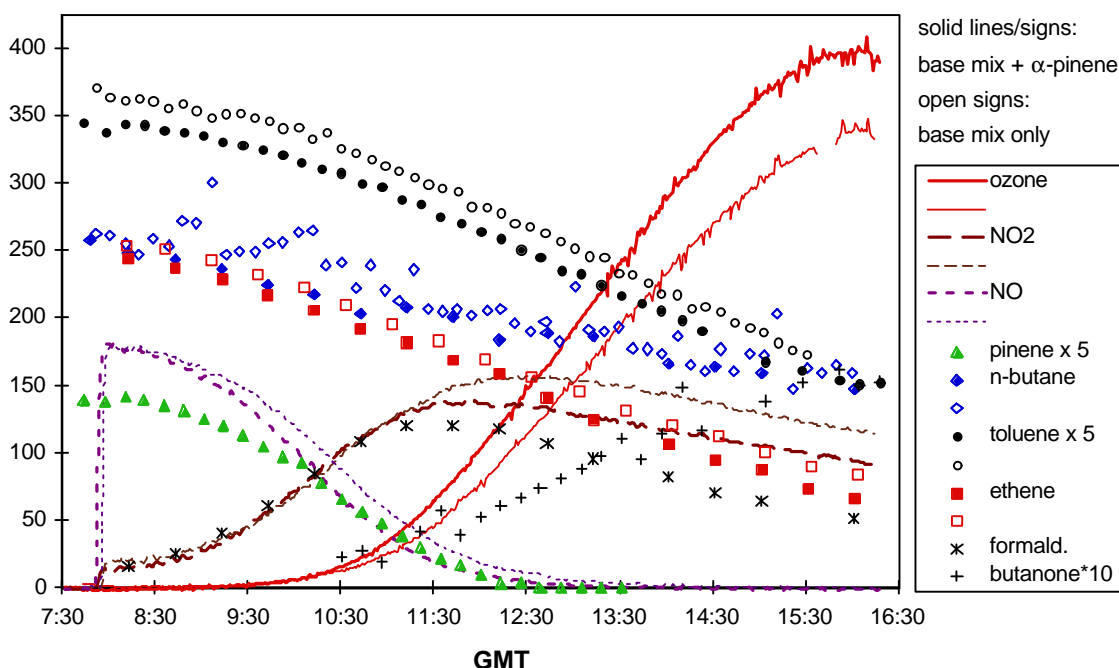
Several smog chamber runs have been carried out in the outdoor simulation chamber EUPHORE in Valencia, Spain (Becker, 1996). A three-component VOC mixture (*base mix*) was chosen as a reference case. The composition of the *base mix* (n-butane, 50%-C, ethene and toluene 25%-C, each) was chosen (1) to represent the proportions of the main VOC classes, alkanes, alkenes and aromatic hydrocarbons, typically measured in relatively polluted ambient air and (2) to deal with compounds whose oxidation pathways are relatively well known, in order to reduce the uncertainties for the modeling of the reference system. By adding relatively small amounts of a fourth VOC of interest, e.g. a biogenic one, changes in the NO<sub>x</sub> transformation and ozone formation relative to the base mix runs should be observed. This experimental approach is mainly based on similar experiments by Carter *et al.*, 1995, who used indoor smog chambers with artificial light sources.

In this contribution we report on experiments with isoprene,  $\alpha$ -pinene, limonene and the potential fuel additive di-ethoxy methane (DEM) as additives to the base mix. The initial carbon and NO<sub>x</sub> concentrations of 2 ppm-C and 200 ppb, respectively, as well as the proportions of the base mix VOCs were kept constant in all experiments. In every experiment the mixture was exposed to sunlight for at least 7 h, centered around midday. Besides the reacting VOCs, ozone, NO and NO<sub>2</sub>, also the concentrations of a number of reaction products could be measured time-resolved, e.g. formaldehyde, 2-butanone, methyl vinyl ketone, methacrolein and PAN.

## Experimental Results

In Fig. 1 the concentration-time profiles of several species from two experiments, a *base case* and one with added  $\alpha$ -pinene, are plotted for comparison. The experiments were run on two consecutive days with clear sky conditions so that light, temperature and chamber conditions are virtually equal during both runs.

The most obvious difference lies in the enhanced ozone formation in the  $\alpha$ -pinene experiment, which continues even after the  $\alpha$ -pinene has completely reacted. The accurate data analysis revealed that in the  $\alpha$ -pinene experiment, compared to the base run, [OH] is slightly suppressed in the beginning of the run, when the overall OH-reactivity is substantially increased due to the highly reactive  $\alpha$ -pinene, but significantly increased in the second half of the experiment, after the  $\alpha$ -pinene had reacted.

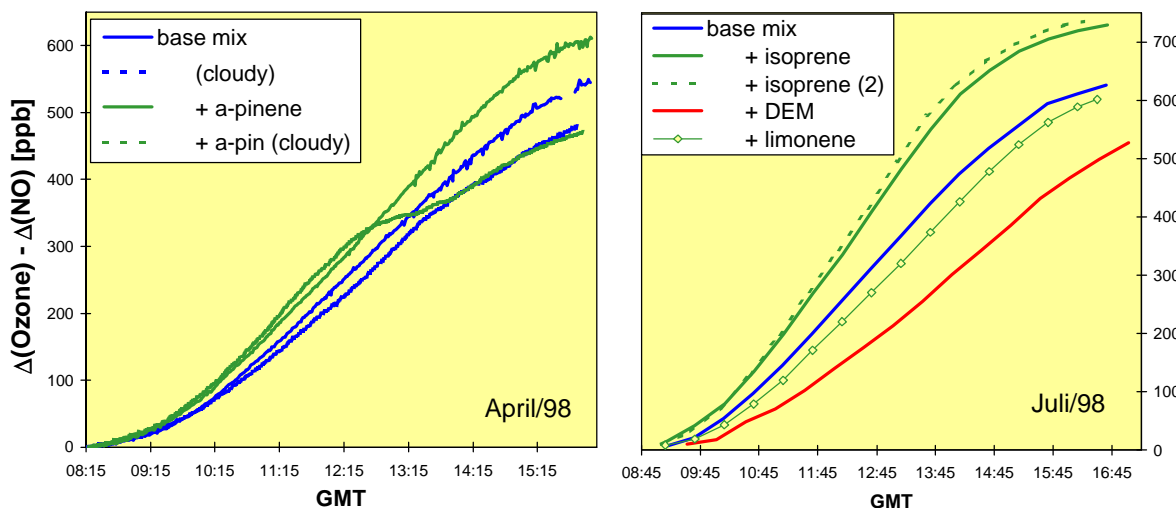


**Fig. 1:** Comparison of concentration/time profiles from two EUPHORE photosmog runs (April, 1998): Base mix +  $\alpha$ -pinene (thick lines/signs) - base mix only (open signs / thin lines)

Fig. 2 (left) shows the  $\Delta[\text{O}_3] - \Delta[\text{NO}]$  (corrected for dilution losses) from four runs, two with the base mix and two with  $\alpha$ -pinene added. This quantity serves as a measure for the total amount of NO oxidized to NO<sub>2</sub> by peroxy radicals, the step directly linked to ozone production. Besides the experiments from Fig. 1, two experiments were evaluated which were characterized by partly cloudy conditions with significantly reduced radiation intensities. This reduction leads to a prompt decrease of the oxidation rate, showing that one or several photolysis reactions influence the radical formation. As the water vapor concentration in the experiments is very low (ca. 0.2 mbar), the photolysis of O<sub>3</sub>, which is the important step in the atmosphere, is not likely to be of importance in the EUPHORE chamber.

Nevertheless the increased ozone formation rate in the  $\alpha$ -pinene runs is obvious. This is even clearer in the case of isoprene, from the respective plot shown in Fig. 2 (right). Here five runs from July, 98 are displayed, made under very similar (clear sky) conditions. Whereas the

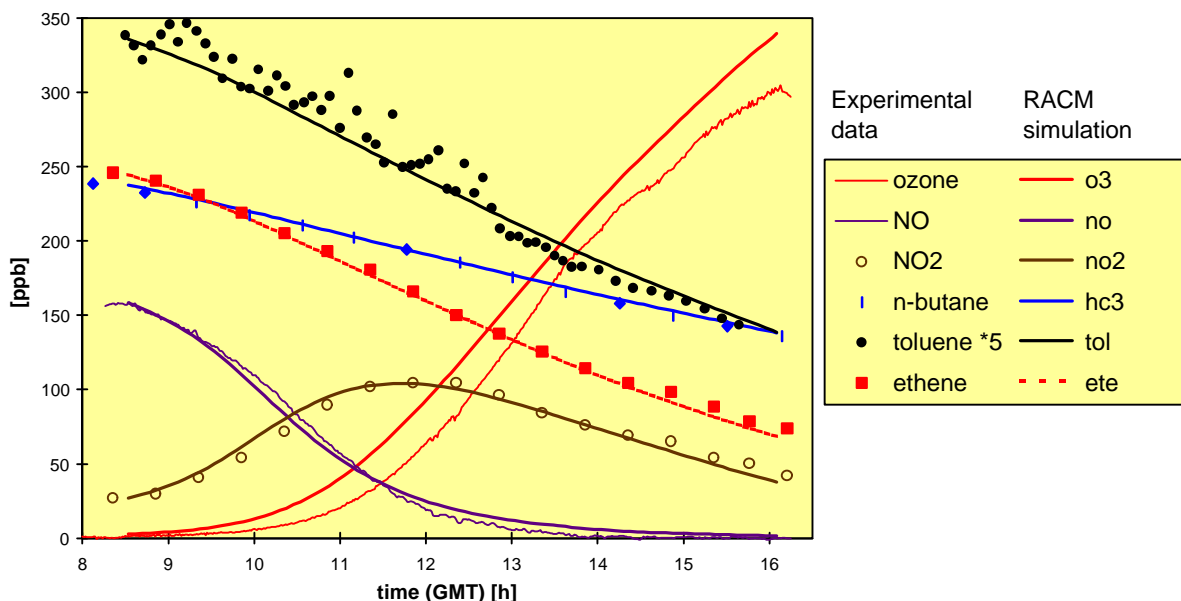
addition of limonene does not lead to a significant deviation from the base-mix, the experiment with DEM is characterized by a strong decrease in the ozone formation rate.



**Fig. 2:** Comparison of  $\Delta[O_3]-\Delta[NO]$  in base mix runs with  $\alpha$ -pinene (left) and isoprene, limonene and di-ethoxy methane (DEM) experiments (right), respectively. The left plot also shows the influence of variations in the sunlight intensity.

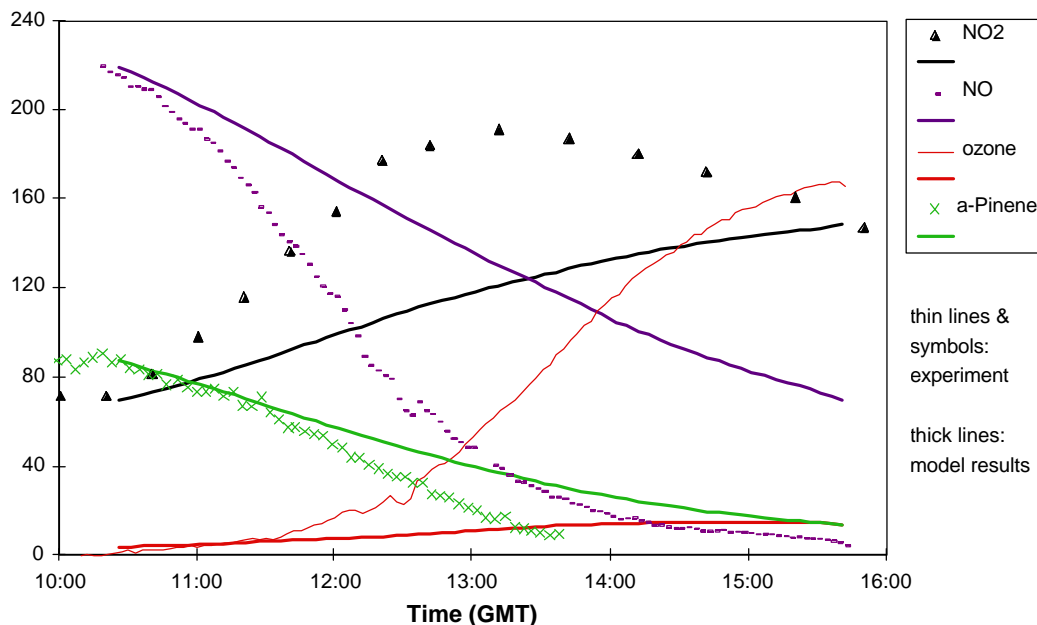
**Simulation Results**

A number of experiments including several base mix runs, experiments with added isoprene and  $\alpha$ -pinene and one experiment with  $\alpha$ -pinene as single VOC were simulated with the RACM mechanism from Stockwell et al., 1997. Results from the model runs, compared with the measured concentrations are displayed in Figs. 3 - 5.

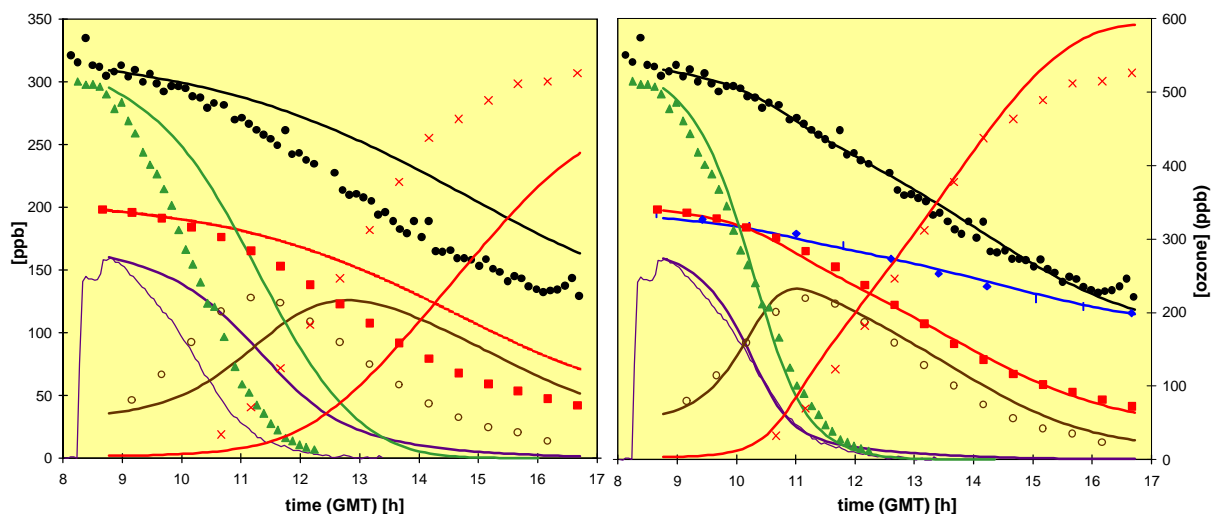


**Fig. 3:** EUPHORE - photosmog run: *Base mix* (n-butane, ethene, toluene: 2 ppm-C + 200 ppb  $NO_x$ ). Comparison of experimental with simulated data (RACM).

No "artificial" sources of OH ("chamber-wall source") were used in the simulations. Only small amounts of HONO (< 1 ppb) were assumed to be present initially.



**Fig. 4:** EUPHORE - photosmog run: 90 ppb  $\alpha$ -pinene + 280 ppb  $\text{NO}_x$ . Comparison of experimental with simulated data (RACM).



**Fig. 5:** Photosmog experiment with base-mix + isoprene. Comparison of experimental and simulated concentration time plots. Left plot: Original RACM, right: modified RACM code (see text and Table 1).

Whereas excellent agreement between measured and simulated concentrations (of VOCs,  $\text{NO}_x$  and ozone) was observed for experiments with the base-mix (Fig. 3), RACM clearly underpredicts the reactivity in experiments with added isoprene (Fig. 5). Therefore parts of the RACM dealing with isoprene have been modified and updated using results from recent laboratory studies. An improved simulation of the measured data is obtained for all runs investigated so far (Fig. 5, right).

Only the product formation from the reaction of isoprene with OH has been changed so far, since this is the only relevant reaction under the experimental conditions. The strongest influence showed the decrease of the organic nitrate yield (from 0.153 to 0.044) and the increase of the reactivity of the reaction products (see Table 1).

**Table 1:** Modification of the product formation from isoprene + OH in the RACM

Product	Product Yield		Explanation
	<i>RACM</i> <sup>a</sup>	new <sup>b</sup>	
MACR	0.446	0.57	methacrolein (new: C <sub>4</sub> -carbonyls)
OLT	0.354	-	terminal alkene (instead of <i>MVK</i> )
OLI	-	0.43	internal alkene
HCHO	0.606	0.57	formaldehyde
ONIT	0.153	0.044	organic nitrates

a) Stockwell et al. 97, based on data from Paulson et al. 92; b) results from Tuazon and Atkinson, 91; Kwok et al. 95; Chen et al. 98; Ruppert and Becker, *in press*

It has to be stressed that no attempts had been made to fit any of the modified variables in the mechanism to the EUPHORE data, but that the changes introduced in the RACM are purely based on independent laboratory studies. The modifications were introduced without increasing the number of species or reactions in the RACM.

### Summary and Conclusions

- ❑ Addition of  $\alpha$ -pinene / isoprene to the base mix increases the rate of ozone formation (amount of ozone formed + NO oxidized in a certain time) (reactivity increase!). Addition of di-ethoxy methane shows the opposite effect. If this is valid also under different conditions (e.g. VOC / NO<sub>x</sub>-ratio) needs to be tested in future experiments.
- ❑  $\alpha$ -Pinene and isoprene increase the average OH-concentration (possibly decrease at the beginning of the experiment, due to increased initial OH-reactivity).
- ❑ Butanone was measured as product from n-butane + OH with a molar yield of 35±5 %. Further reaction products which could be measured in the experiments by GC or FTIR include methacrolein, methyl vinyl ketone (from isoprene), formaldehyde, acetaldehyde, HNO<sub>3</sub> and PAN.

### Simulations with RACM:

- ❑ No chamber specific reactions, besides a constant and known dilution factor, had to be introduced into the mechanism. Especially, no artificial OH-source was required, except a small and realistic initial HONO concentration. Further chamber characterization studies are required to justify this treatment.
- ❑ Base mix runs could be reasonably simulated.

- ❑ RACM severely underestimates the ozone formation (and NO to NO<sub>2</sub> conversion) in experiments with added isoprene and in a *pure*  $\alpha$ -pinene experiment (Fig. 4), possibly due to underestimation of the reactivity of the oxidation products from  $\alpha$ -pinene.
- ❑ Mechanism modifications according to recent laboratory results improve the mechanism performance.

## Acknowledgements

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## References

- Becker, K.H. (ed), The European Photoreactor EUPHORE. *EC final report EV5V-CT92-0059*, Wuppertal (1996).
- Biesenthal, T.A., J.W. Bottenheim, P.B. Shepson, S.-M. Li and P.C. Brickell; The chemistry of biogenic hydrocarbons at a rural site in eastern Canada, *J. Geophys. Res.* **103** (1998) 25487-25498.
- Carter, W.P.L., J.A. Pierce, D. Luo and I.L. Malkina; Environmental chamber study of maximum incremental reactivities of volatile organic compounds, *Atmos. Environ.* **29** (1995) 2499-2511.
- Chen, X., D. Hulbert and P.B. Shepson; Measurement of the organic nitrate yield from OH reaction with isoprene, *J. Geophys. Res.* **103** (1998) 25563-25568.
- Kwok, E.S.C., R. Atkinson and J. Arey; Observation of hydroxycarbonyls from the OH radical-initiated reaction of isoprene, *Environ. Sci. Technol.* **29** (1995) 2467-2469.
- Paulson, S.E., R.C. Flagan and J.H. Seinfeld; Atmospheric photooxidation of isoprene. Part I: The hydroxyl radical and ground state atomic oxygen reactions, *Int. J. Chem. Kinet.* **24** (1992) 79-101.
- Roberts, J.M., et al.; Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville intensives of the Southern Oxidant Study: implications for regional ozone production from biogenic hydrocarbons, *J. Geophys. Res.* **103** (1998) 22473-22490.
- Ruppert, L. and K.H. Becker; A product study of the OH radical-initiated oxidation of isoprene: Formation of C<sub>5</sub>-unsaturated diols, *Atmos. Environ.* in press.
- Staffelbach, T. et al.; Photochemical oxidant formation over southern Switzerland. 1. Results from summer 1994, *J. Geophys. Res.* **102** (1997) 23345-23362.
- Stockwell, W.R., F. Kirchner, M. Kuhn and St. Seefeld; A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.* **102** (1997) 25847-25879.
- Tuazon, E.C. and R. Atkinson; A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO<sub>x</sub>, *Int. J. Chem. Kinet.* **22** (1990) 1221-1236.