

Measurement of Peroxy Radicals in the European Photoreactor EUPHORE

First results from the project SAMPLER

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Introduction

Peroxy radicals (HO_2 and RO_2) are key species in the photochemical formation of ozone, peroxides and organic nitrates in the troposphere. They arise from the oxidation of volatile organic compounds (VOC) and CO by hydroxyl radicals (OH). The reaction of peroxy radicals with NO is the rate-limiting step of O_3 production. Recent literature data for the rate coefficients for this reaction disagree by a factor of two or more (Peeters *et al.*, 1992, Eberhard and Howard, 1997). We studied the oxidation of i-butane (100 ppb) in the presence of 10 ppb NO_x and 110 ppb HCHO in the European Photoreactor EUPHORE. Measurements of peroxy radicals were made with two methods: Matrix-Isolation followed by electron spin resonance MIESR and Chemical amplification CA. The results are compared to model calculations.

Experimental

The experimental procedure was as follows: After flushing the chamber for at least 12 hours with purified air, an FTIR background spectrum was recorded. Then, the reagent gases NO_2 and i-butane and the tracer SF_6 were introduced in the chamber by adding known amounts of the pure gases into a gas flow of 2 sL/min which was fed into the chamber. HCHO was added by evaporating a known amount of paraformaldehyde into the same gas flow. After allowing for mixing, the initial concentrations were determined. Then, the chamber was exposed to sunlight and the temporal evolution followed for about 6 hours. Table 1 gives an overview over the initial conditions and the instrumentation.

Table 1 Initial conditions and instrumentation

Species	Initial value	Instrumentation	Time resolution	Detection limit
i-butane	100 ppb	FTIR	10 minutes	3 ppb
NO, NO_2	11 ppb	PC-CLD	1 minute	100 ppt
HCHO	110 ppb	FTIR	10 minutes	3 ppb
SF_6	26 ppb	FTIR	10 minutes	0.5 ppb
O_3	0	UV-Absorption	1 minute	2 ppb
HO_2 , RO_2 , NO_2	0	MIESR	30 minutes	2.5 ppt
(HO_2 + RO_2)		CA	1 minute	2 ppt

HCHO, i-butane and SF_6 were measured with FTIR. NO was measured with chemiluminescence. NO_2 was converted to NO by a photolytic converter and measured by chemiluminescence. In

addition, NO₂ was measured by MIESR. O₃ was measured using UV-absorption. The photolysis rate of NO₂, J(NO₂), was measured using two 2π filterradiometers pointing upward and downward, respectively, whose spectral sensitivity matches the effective cross section of NO₂. Measurements of peroxy radicals were achieved using two methods: Matrix-Isolation Electron Spin Resonance MIESR (Mihelcic *et al.*, 1985, 1990) and Chemical Amplification CA (Cantrell and Stedman, 1982, Hastie *et al.*, 1991, Heitlinger, 1997). MIESR is an absolute method which allows speciation of HO₂ and RO₂ (and NO₂ and NO₃). In contrast, the CA is an indirect method which measures the sum of HO₂ and RO₂. The HO₂ calibration source used for calibration was compared to MIESR and agreed within 15% (Heitlinger, 1997). For further details of the MIESR method, see Mihelcic *et al.*, 1985, 1990; for details of the CA and calibration source see Heitlinger, 1997. Both instruments were mounted in the same distance from the chamber floor in specially designed flanges.

Data Quality

Figure 1 shows the comparison of the NO₂ values measured by PC-CLD and by MIESR. The high concentrations agree within 2%, whereas the lower concentrations (which were recorded in the presence of ca 80 ppb O₃) are underestimated by PC-CLD by up to 300 ppt (or 15%). This underestimate is presumably caused by the negative O₃ interference in the photolytic converter which reduces the NO₂ conversion efficiency.

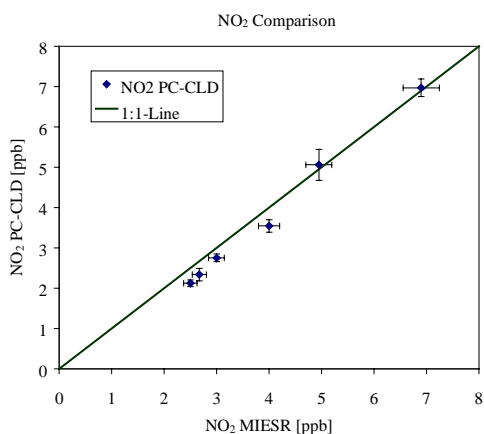


Figure 1 Comparison of NO₂ measured by PC-CLD and NO₂ measured by MIESR. The error bars represent the variability of the NO₂ concentrations during that time. The solid line shows the expected 1:1-behaviour. The higher concentrations agree within 2%, whereas the lower concentrations are underestimated by PC-CLD by up to 300 ppt or 15%.

The calibration of the O₃ measurement was found to agree within 3% with another instrument which was calibrated in Jülich before and after the campaign. The NO measurements are tied to a certified gas mixture cylinder accurate within 2%.

The comparison of the radical measurements is shown in Figure 2. The data agree within 5%, which is due to the fact that the calibration source of the CA was characterised using MIESR (Heitlinger, 1997).

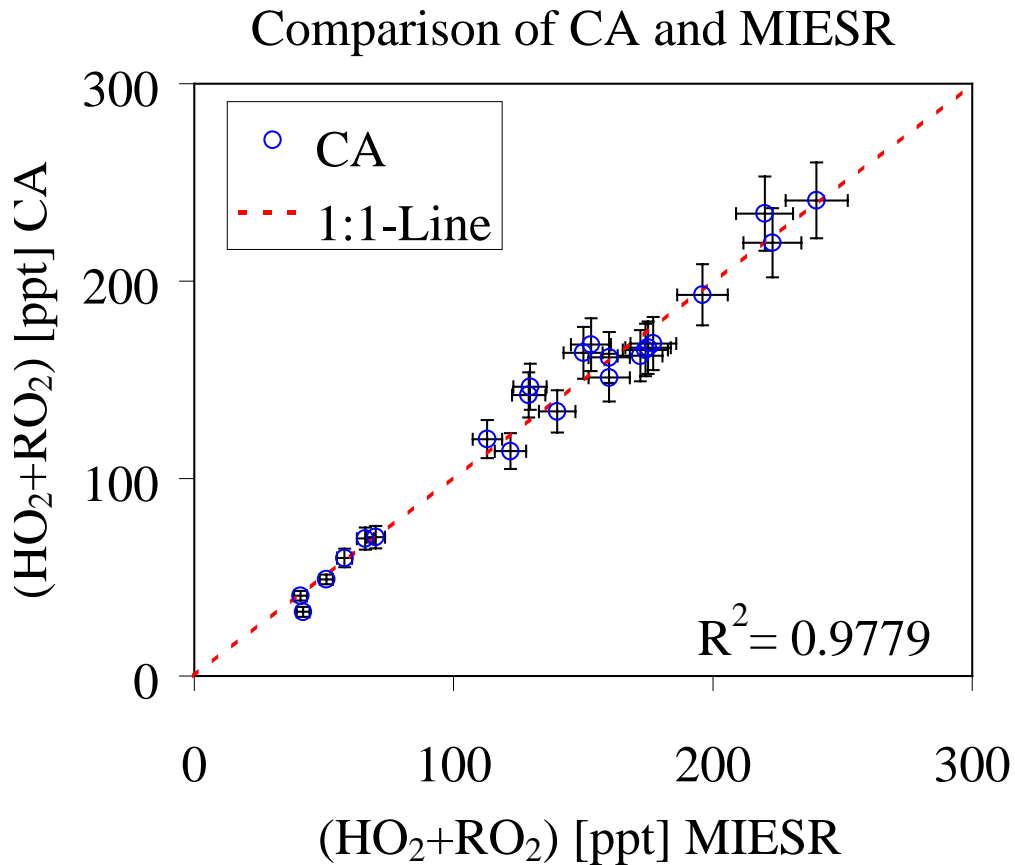


Figure 2 Comparison of the radical measurements by CA and MIESR.

In order to ensure that wall loss of radicals can be neglected, the radical profile in the EUPHORE was checked with the CA by positioning the inlet in several distances from the wall. Figure 3 shows the results of these checks. The red line shows the radical concentrations measured by the CA, the blue line shows the distance between the chamber floor and the inlet of the CA. It can be clearly seen that the position of the inlet has no influence on the measured radical concentrations. The slight increase of the radical concentrations with time is due to the increasing light intensity over that time period.

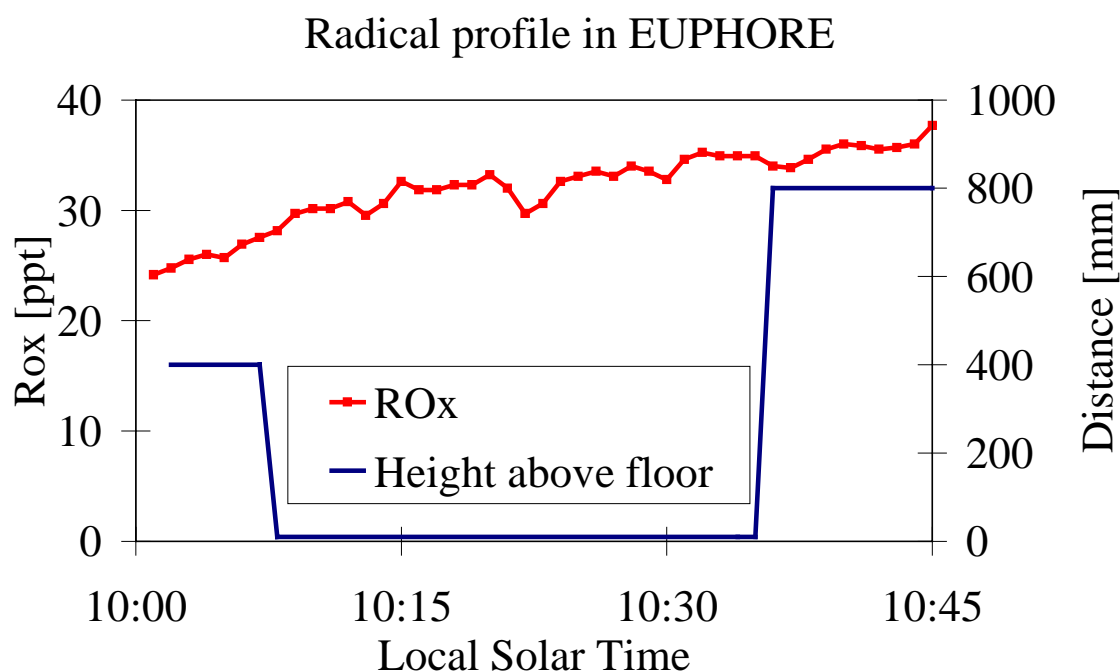


Figure 3 Radical profile in EUPHORE measured with the CA.. The red line shows the radical concentrations measured by the CA, the blue line shows the distance between the chamber floor and the inlet of the CA. The position of the inlet has no influence on the measured radical concentrations. The slight increase of the radical concentrations with time is due to the increasing light intensity over that time period.

Model calculations

In order to compare the measurements with photochemical theory, we made model calculations using the "Master Chemical Mechanism" described by *Jenkin et al., 1997*, with some minor changes as described below.

Procedure for the model calculations

The model was initialised with the initial (dark) conditions for the time of chamber-opening and allowed to equilibrate. A common, constant dilution factor was applied to all species. The magnitude (ca 2%/hour) was chosen to reproduce the measured SF₆ concentrations. Deposition of O₃ and NO₂ to the chamber walls was taken as 2%/hour as derived from the lifetime of O₃ in the chamber (*Wirtz, pers. comm.*). Besides these changes, no forcing of concentrations was applied to the model. Forcing of the photolysis rates was achieved as follows: first, the model was used to calculate the clear-sky photolysis rates as described by *Jenkin et al., 1997*. Then, all photolysis rates were scaled with the ratio of measured J(NO₂) to calculated J(NO₂). The resulting photolysis rates were used for the model calculations. This forcing was applied every minute. This procedure assumes that the light attenuation by clouds is identical for all wavelengths, which is presumably

not true (*Kraus, 1998*). Since we found that the decrease of HCHO was initially strongly overestimated by the model, we decreased $J(\text{HCHO})$ to match the HCHO concentrations.

Mechanistic changes to the model

The rate coefficient for the reaction $\text{OH} + \text{NO}_2$ was taken from Donahue et al., 1997. The influence of the reaction $\text{RO}_2 + \text{NO}$ was studied by performing two different model runs: In model A, we used a rate coefficient of $k=8 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$ as suggested by *Eberhard and Howard, 1997*, in model B, we used $k=4 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$ as measured by *Peeters et al., 1992*.

Results and discussion

Figure 4 shows the time series of the measured species and the results of the model calculations. The red lines represent the measurements performed with the Euphore equipment and the CA, the black lines show the MIESR results. The blue lines represent the standard Model with $k(\text{RO}_2 + \text{NO})= 8 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$; the green lines the standard model with $k(\text{RO}_2 + \text{NO})= 4 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$. The concentrations of HCHO, NO and NO_2 are reproduced very good by the model, agreement is within 5%. The agreement is slightly worse for i-butane (ca 10%), which is underestimated by the model. One possible reasons is a slightly lower rate coefficient for the reaction of i-butane with OH. The radical measurements of the CA reproduce the diurnal variation of RO_x ($=\text{HO}_2+\text{RO}_2$) fairly good, including short-term fluctuations of the RO_x concentrations. The absolute values measured by CA agree well with both the model and the MIESR data. This is not surprising, given the fact that the calibration source of the CA was characterised using MIESR (*Heitlinger et al., 1997*).

Both model runs yield similar values for the sum of HO_2 and RO_2 . However, the split between HO_2 and RO_2 is greatly influenced by a change in the rate coefficient of $\text{RO}_2 + \text{NO}$. Model B ($k= 4 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$) is much closer to the MIESR results, especially for the afternoon values. In addition, the O_3 concentrations predicted by Model B are in much better agreement with the measurements than those of Model A. Our data support the value of $k=4 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$ measured by *Peeters et al., 1992*, for t- $\text{C}_4\text{H}_9\text{O}_2$ (the predominant organic RO_2 in our experiment). The values of $k \cong 8 \cdot 10^{-12} \text{ cm}^3 \text{molek.}^{-1} \text{s}^{-1}$ found by *Eberhard and Howard, 1997*, for this peroxy radical, however, contradict this finding. Therefore, further work on the rate coefficients of this and other RO_2 with NO is required.

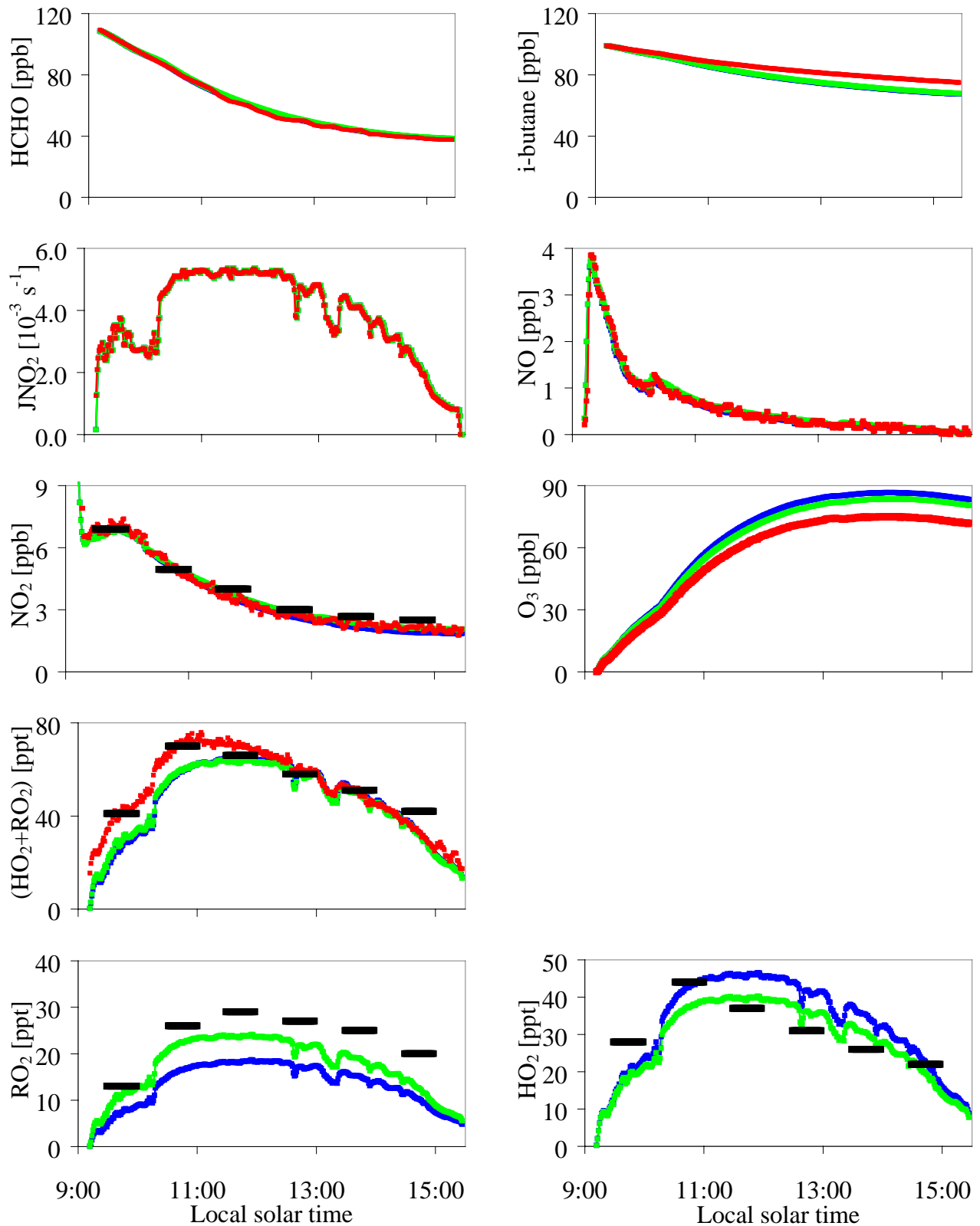


Figure 4

Results of the experiments and model calculations. The red lines represent the measurements of HCHO, i-butane, NO₂, J(NO₂), NO, RO_x and O₃, the black lines the MIESR results. The blue lines represent the standard Model with $k(\text{RO}_2 + \text{NO}) = 8 \cdot 10^{-12} \text{ cm}^3 \text{ molek.}^{-1} \text{ s}^{-1}$; the green lines the standard model with $k(\text{RO}_2 + \text{NO}) = 4 \cdot 10^{-12} \text{ cm}^3 \text{ molek.}^{-1} \text{ s}^{-1}$.

Conclusions

Measurements of HO₂ and RO₂ were conducted successfully for the first time in the EUPHORE. A comparison of the results with model calculations support the value of *Peeters et al., 1992*, for the rate coefficient of t-C₄H₉O₂ + NO, namely $4 \cdot 10^{-12} \text{ cm}^3 \text{ molek.}^{-1} \text{ s}^{-1}$. Future work will focus on the radical chemistry of alkenes and aromatics.

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