Airborne observations of peroxy radicals during the EMeRGGe campaign in Europe

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Abstract. In this study, airborne measurements of the sum of hydroperoxyl (HO$_2$) and organic peroxy (RO$_2$) radicals that react with nitrogen monoxide (NO) to produce nitrogen dioxide, (NO$_2$), coupled with actinometry and other key trace gases measurements, have been used to test the current understanding of the fast photochemistry in the outflow of major population centres. The measurements were made during the airborne campaign of the EMeRGGe (Effect of Megacities on the transport and transformation of pollutants on the Regional to Global scales) project in Europe on-board the High Altitude Long range research aircraft (HALO). The measurements of RO$_2^+$ on HALO were made using the in-situ instrument Peroxy Radical Chemical Enhancement and Absorption Spectrometer (PeRCEAS). RO$_2^+$ is to a good approximation the sum of peroxy radicals reacting with NO to produce NO$_2$. RO$_2^+$ mixing ratios up to 120 pptv were observed in air masses of different origins and composition under different local actinometrical conditions during seven HALO research flights in July 2017 over Europe. Radial production rates were estimated using knowledge of the photolysis frequencies and the RO$_2^+$ precursor concentrations measured on-board, as well as the relevant rate coefficients. Generally, high RO$_2^+$ concentrations were measured in air masses with high production rates. In the airmasses investigated RO$_2^+$ is primarily produced by the reaction of O$_1$D with water vapour, and the photolysis of nitrous acid (HONO) and of the oxygenated volatile organic compounds (OVOC, e.g., formaldehyde (HCHO), and glyoxal (CHOCHO)). Due to their short lifetime in most environments, the RO$_2^+$ concentrations are expected to be in a photostationary steady state (PSS), i.e., it is assumed a balance between production and loss rates. The RO$_2^+$ production and loss rates and the suitability of PSS assumptions to estimate the RO$_2^+$ mixing ratios and variability during the airborne observations are discussed. The PSS assumption for RO$_2^+$ is considered robust enough to calculate RO$_2^+$ mixing ratios for most conditions encountered in the air masses measured. The similarities and discrepancies between measured and PSS calculated RO$_2^+$ mixing ratios are discussed. The dominant terminating processes for RO$_2^+$ in the pollution plumes measured up to 2000 m are the formation of nitrous acid, nitric acid and organic nitrates. Above 2000 m, HO$_2$ – HO$_2$ and HO$_2$ – RO$_2$ reactions dominate the RO$_2^+$ removal. RO$_2^+$ calculations by the PSS analytical expression inside the pollution plumes probed often underestimated the measurements. The underestimation is attributed to the limitations of the PSS equation used for the analysis. In particular, this expression does not account for the yields of RO$_2^+$ from the oxidation and photolysis of volatile organic compounds, VOCs, and OVOCs other than those measured during the EMeRGGe research flights in Europe. In air masses with NO mixing ratios ≤ 50 pptv and low VOC/NO ratios, the overestimation of the RO$_2^+$ measured observed may be caused by the formation of H$_2$O and O$_2$ from OH and HO$_2$, being about 4 times faster than the rate of the OH oxidation reaction of the dominant OVOCs considered.
1. Introduction

Hydroperoxyl (HO$_2$) and organic peroxo (RO$_2$, where R stands for any organic group) radicals are reactive species that play a key role in the chemistry of the troposphere. In combination with the hydroxyl (OH) radical, HO$_2$ and RO$_2$ take part in rapid chemical processes that control the lifetime of many key trace constituents in the troposphere. Examples of key tropospheric processes involving HO$_2$ and RO$_2$ are as follows:

- the catalytic cycles which produce and destroy ozone (O$_3$)
- the generation of inorganic acids, which are precursors of aerosol (e.g., sulphuric acid, H$_2$SO$_4$) and important chemical constituents (e.g., nitric acid, HNO$_3$) in both summer and winter smog
- the generation of organic acids; the production of hygroscopic hydrogen peroxide (H$_2$O$_2$) and organic peroxides (ROOH), which enter aerosol and cloud droplets
- the generation of organic peroxy nitrates (RO$_2$NO$_2$), peroxyacetyl nitrate (CH$_3$COO$_2$NO, PAN) and other summer smog constituents.

The abundance of HO$_2$ and RO$_2$ in the free troposphere has a non-linear and complex dependency on photochemistry, initiated by solar actinic radiation, and on the concentration of the precursors, such as carbon monoxide (CO), volatile organic compounds (VOCs), and peroxides. It also strongly depends on the amounts of nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$) due to the gas-phase reactions of NO and NO$_2$ with the OH and organic oxy (RO) radicals formed during the radical interconversion. The main production and loss processes of HO$_2$ and RO$_2$ in the troposphere are summarised as follows:

a) Production processes of HO$_2$ and RO$_2$

\[
\begin{align*}
O_3 + \text{hv} (\lambda < 320 \text{ nm}) & \rightarrow O(^1D) + O_2 & \text{(R1)} \\
O(^1D) + H_2O & \rightarrow 2OH & \text{(R2a)} \\
O(^1D) + N_2 & \rightarrow O(^3P) + N_2 & \text{(R2b)} \\
O(^1D) + O_2 & \rightarrow O(^3P) + O_2 & \text{(R2c)} \\
\text{HONO} + \text{hv} (\lambda \leq 400 \text{ nm}) & \rightarrow \text{OH} + \text{NO} & \text{(R3)} \\
H_2O_2 + \text{hv} & \rightarrow 2\text{OH} & \text{(R4)} \\
\text{OH} + O_3 & \rightarrow \text{HO}_2 + O_2 & \text{(R5)} \\
\text{OH} + \text{CO} + O_2 & \rightarrow \text{HO}_2 + \text{CO}_2 & \text{(R6)} \\
(*) \text{OH} + CH_4 + O_2 & \rightarrow CH_3O_2 + H_2O & \text{(R7)} \\
(**) \text{HCHO} + \text{hv} (\lambda < 340 \text{ nm}) + 2O_2 & \rightarrow 2\text{HO}_2 + \text{CO} & \text{(R8)} \\
(*)(**) \text{CH}_3\text{CHO} + \text{hv} (\lambda < 340 \text{ nm}) + 2O_2 & \rightarrow \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{CO} & \text{(R9)}
\end{align*}
\]

(*) The CH$_3$ produced from the oxidation of CH$_4$ or the photolysis of VOCs further reacts with O$_2$ to form CH$_3$O$_2$. The net or overall reaction is used because the formation of CH$_3$O$_2$ is much faster than the CH$_3$ formation due to the high amount of O$_2$ present in the atmosphere.

(**) H and CHO formed through the VOC photolysis further react with O$_2$ to form HO$_2$. The net reaction is used, because the formation of HO$_2$ is much faster than the H and CHO formation due to the high amount of O$_2$ present in the atmosphere.
\[ (**\) \text{CH}_3\text{C(O)CH}_3 + h\nu (\lambda < 340 \text{ nm}) + 2\text{O}_2 \rightarrow 2 \text{CH}_3\text{O}_2 + \text{CO} \quad (\text{R10}) \]
\[ (**\) \text{CHOCHO} + h\nu + 2\text{O}_2 \rightarrow 2\text{HO}_2 + 2\text{CO} \quad (\text{R11}) \]

75 \[ \text{VOCs} + \text{OH} \rightarrow \text{OH} + \text{HO}_2 + \text{RO}_2 \text{ and other oxidation products} \quad (\text{R12}) \]

alkenes + \text{O}_3 \rightarrow \text{OH} + \text{RO}_2 + \text{other oxidation products} \quad (\text{R13})

b) Loss processes of \text{HO}_2 \text{ and RO}_2

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (\text{R14}) \]
\[ \text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2 \quad (\text{R15}) \]
\[ \text{RO}_2 + \text{RO}_2 \rightarrow \text{RO} + \text{RO} + \text{O}_2 \quad (\text{R16a}) \]
\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (\text{R17}) \]
\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (\text{R18}) \]
\[ \text{OH} + \text{NO} \rightarrow \text{HONO} \quad (\text{R19}) \]
\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \quad (\text{R20}) \]
\[ \text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \quad (\text{R21}) \]
\[ \text{RO} + \text{NO} \rightarrow \text{RONO} \quad (\text{R22}) \]

In addition, \text{HO}_2 \text{ and RO}_2 \text{ participate in radical interconversion reactions such as:}

\[ \text{RO}_2 + \text{RO}_2 \rightarrow \text{RO} + \text{RO} + \text{O}_2 \quad (\text{R16b}) \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (\text{R23}) \]
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad (\text{R24}) \]
\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \quad (\text{R25a}) \]
\[ \text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2 \quad (\text{R25b}) \]
\[ \text{RO} + \text{O}_2 \rightarrow \text{R}_{27} \cdot \text{O} + \text{HO}_2 \quad (\text{R26}) \]

95 Reactions R23 and R25a are two of the most important reactions in the troposphere as they lead to \text{O}_3 \text{ formation via the reactions R27 and R28. The rate of the reaction R22 in the atmosphere compared to that of reaction R26 is negligible.}

\((**\) H and CHO formed through the VOC photolysis further react with \text{O}_2 \text{ to form HO}_2. The net reaction is used, because the formation of HO}_2 \text{ is much faster than the H and CHO formation due to the high amount of O}_2 \text{ present in the atmosphere.} \)
The sum of HO$_2$ and RO$_2$ that react with NO to produce NO$_2$ can be estimated by assuming that the interconversion of NO to NO$_2$ reaches a photostationary steady-state (PSS), in which production and loss of NO$_2$ are to a good approximation equal.

The PSS assumption for [NO$_2$] in the following mechanism (reactions R23 to R29) leads to Eq. 1

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{RO}_2 + \text{NO} + \text{O}_2 & \rightarrow \text{R}_\text{th}_1\text{O} + \text{NO}_2 + \text{HO}_2 \\
\text{NO}_2 + \text{hv} (\lambda < 400 \text{ nm}) & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3 \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
[\text{HO}_2 + \text{RO}_2]_{\text{PSS}} &= \frac{k_{\text{NO}+\text{O}_2}}{k_{\text{NO}+(\text{HO}_2+\text{RO}_2)}} \left( \frac{j_{\text{NO}_2}[\text{NO}_2]}{k_{\text{NO}+\text{O}_2}[\text{NO}]} - [\text{O}_3] \right) \quad (\text{Eq. 1})
\end{align*}
\]

where $j_{\text{NO}_2}$ is the photolysis frequency of NO$_2$; $k_{\text{NO}+\text{O}_2}$ (1.9×10^{-14} cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298K and 1 atm.) is the rate coefficient of the reaction of NO with O$_3$ and $k_{\text{NO}+(\text{HO}_2+\text{RO}_2)}$ is usually estimated for the most abundant peroxy radicals HO$_2$ and CH$_3$O$_2$ by assuming a 1:1 HO$_2$ to CH$_3$O$_2$ ratio and averaging the $k_{\text{NO}+\text{HO}_2}$ (8.2×10^{-12} cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298K and 1 atm.) and $k_{\text{NO}+\text{CH}_3\text{O}_2}$ (7.7×10^{-12} cm$^3$ molecules$^{-1}$ s$^{-1}$ at 298K and 1 atm.) rate coefficients for the reaction with NO. As noted by Parrish et al. (1986), the PSS assumption for NO$_2$ requires conditions with sufficient and stable solar irradiation, ensuring stable NO$_2$ photolysis rates ($j_{\text{NO}_2}$).

The radical calculation made on the assumption of the NO$_2$ steady state is very sensitive to the accuracy of the NO$_2$ to NO ratio and the O$_3$ measurements. The comparison of [HO$_2$ + RO$_2$]$_{\text{PSS}}$ calculated using Eq. 1 with ground-based (e.g., Ridley et al., 1992; Cantrell et al., 1997; Carpenter et al., 1998; Volz-Thomas et al., 2003), and airborne measurements, has shown in the past different degrees of agreement. The underestimations and overestimations found in air masses with different chemical compositions are not well understood. For the case of airborne measurements, the NO$_2$ steady state calculation generally overestimates the measured peroxy radicals (Cantrell et al., 2003a, 2003b). The differences observed could not be attributed to systematic changes in NO, altitude, water vapour and temperature, although these variables are often correlated. The NO to NO$_2$ ratio calculated from NO measured using in-situ technique and NO$_2$ measured using remote sensing (more detail about the measurement techniques is given in Table 1) used in this study is considered to have a sufficiently large error. So, the NO$_2$ steady state approach is not accurate enough to calculate [HO$_2$+RO$_2$] for the measurements considered in this study.

Ground-based (Mihelcic et al., 2003; Kanaya et al., 2007, 2012; Elshorbany et al., 2012; Lu et al., 2012, 2013; Tan et al., 2017, 2018; Whalley et al., 2018, 2021; Lew et al., 2020) and airborne (Crawford et al., 1999; Tan et al., 2001; Cantrell et al., 2003b) measurements have also been compared with model simulations of HO$_2$ and RO$_2$. The discrepancies encountered depend upon the chemical composition of the air mass and the chemical mechanisms and constraints used in the model simulations. Recently, Tan et al., 2019 and Whalley et al., 2021 reported experimental radical budget calculations using PSS assumption for OH, HO$_2$ and RO$_2$ together with the published reaction rate coefficients of the reactions (R1 to R26), which control OH, HO$_2$ and RO$_2$ in the lower troposphere, and the ground-based measurements of all relevant reactants and photolysis frequencies. In this study, a similar approach has been used, i.e., the sum of HO$_2$ and RO$_2$ is assumed to be in PSS, to calculate the amount of peroxy radicals in the air masses measured on-board of the High Altitude Long range (HALO) research aircraft over Europe during the first campaign of the EMeRGe (Effect of Megacities on the transport and transformation of pollutants on the Regional to Global scales) project. The available on-board measurements of RO$_2^*$ are defined as the total sum of OH, RO and peroxy radicals (i.e., RO$_2^* = \text{OH} + \sum \text{RO}$).
+ \text{HO}_2 + \sum \text{RO}_2$, where \text{RO}_2 are the organic peroxy radicals producing \text{NO}_2 in their reaction with \text{NO}. As the amount of \text{OH} and \text{RO} is much smaller, \text{RO}_2^* to a good approximation is the sum of \text{HO}_2 and those \text{RO}_2 radicals that react with \text{NO} to produce \text{NO}_2. For the calculation, \text{RO}_2^* is assumed to be in PSS, and an analytical expression is developed with a manageable degree of complexity to estimate the concentration and mixing ratios of \text{RO}_2^*. The simultaneous on-board measurements of trace gases and photolysis frequencies are used to constrain the estimate of the \text{RO}_2^* concentration.

In contrast to other experimental deployments, the concentrations and/or mixing ratios of the majority of the key species involved in reactions R1 to R26 were continuously measured on-board HALO during the EMeRGe campaign. This enables the use of a large number of measurements to constrain the PSS calculation of \text{RO}_2^*. Consequently, this data set provides an excellent opportunity to gain deeper insight into the source and sink reactions of \text{RO}_2^* and the applicability of the PSS assumption for the different pollution regimes and related weather conditions in the free troposphere.

2. **EMeRGe field campaign in Europe**

The overarching objective of the EMeRGe project is to test and improve the current understanding of the photochemical and heterogeneous processing of pollution outflows from major population centres (MPCs) and their impact on the atmosphere. Two intensive observational periods (IOP) were carried out to investigate selected European and Asian MPC outflows. The European IOP took place from 10 to 28 July 2017 (http://www.iup.uni-bremen.de/emerge/home/home.html). An extensive set of in-situ and remote-sensing airborne measurements of trace gases and aerosol particles were made on-board the HALO aircraft (see www.halo-spp.de) along flight tracks in the lower layers of the troposphere from northwest Europe to the Mediterranean region.

During EMeRGe in Europe, HALO made a total of 53 flight hours distributed over seven flights to investigate the chemical composition of the outflows from the target MPCs: London, Paris, Benelux/ Ruhr metropolitan area, Po Valley, and urban agglomerations such as Rome, Madrid, and Barcelona. The flight tracks are shown in Fig. 1. All measurement flights started from the aircraft hangar at the DLR in Oberpfaffenhofen, southwest of Munich, Germany. To achieve the scientific goals, 60 % of the flights flew at altitudes below 3000 m. Vertical profiles of trace constituents were typically made by keeping the HALO altitude constant at different at flight levels upwind and downwind of the target MPCs. The flights are named E-EU-FN, where E stands for EMeRGe, EU for Europe, and FN is the two-digit flight number. More details about the EMeRGe IOP in Europe and the set of instruments deployed on-board the HALO aircraft are described elsewhere (Andrés Hernández et al., 2022).
3. PeRCEAS and other instruments on-board HALO during EMeRGe

The RO$_2^*$ measurements on-board the HALO research aircraft during EMeRGe were made using the Peroxy Radical Chemical Enhancement and Absorption Spectrometer (PeRCEAS). PeRCEAS combines the Peroxy Radical Chemical Amplification (PeRCA) and Cavity Ring-Down Spectroscopy (CRDS) techniques in a dual-channel instrument. Each channel has a separate chemical reactor and detector, which operate alternatively in both background and amplification modes to account for the rapid background variations during airborne measurements. In both modes NO is continuously added to the air sampled at the reactor, while CO is only added in the amplification mode to initiate the chain conversion of RO$_2^*$ into NO$_2$. In the amplification mode, the sum of the NO$_2$ produced from ambient RO$_2^*$ through the chain reaction, the ambient NO$_2$, the NO$_2$ produced from the ambient O$_3$ – NO reagent gas reaction and the NO$_2$ produced in the inlet from any other sources (e.g., thermal decomposition of PAN) is measured. In the background mode, the sum of the ambient NO$_2$, the NO$_2$ produced from the ambient O$_3$ – NO reagent gas reaction and NO$_2$ produced in the inlet from any other sources is measured. The RO$_2^*$ is retrieved by dividing the difference in NO$_2$ concentration ($\Delta$NO$_2$) between amplification and background mode by the conversion efficiency of RO$_2^*$ to NO$_2$, which is referred to as eCL (effective chain length). The PeRCEAS instrument and its specifications have been described in detail elsewhere (Horstjann et al., 2014, George et al., 2020).

The two chemical reactors for sampling the ambient air are part of the DUal channel Airborne peroxy radical Chemical Amplifier (DUALER) inlet installed inside a pylon located on the outside of the HALO fuselage. During the EMeRGe campaign in Europe, a reagent gas mixing ratio of 30 ppmv NO ([NO] = 1.46 x 10$^{14}$ molecules cm$^{-3}$ at 296 K, 200 mbar) and of 9 % CO ([CO] = 4.4 x 10$^{17}$ molecules cm$^{-3}$ at 296 K, 200 mbar) were added to the sample flow for the chemical conversion of RO$_2^*$ to NO$_2$. The DUALER inlet was operated at an internal pressure of 200 mbar to achieve stable chemical conversion. The HO$_2$ and RO$_2$ detection...
sensitivity depends on the rates of loss of HO$_2$ and RO$_2$ by the reactions R19 and R22. The latter depend on the concentration of the reagent gas NO added and the reactions rate coefficients, where $k_{22}$ is larger than $k_{19}$. The average eCL for a 1:1 HO$_2$ to CH$_3$O$_2$ mixture under the DUALER conditions during the campaign in Europe was determined to be 50 ± 8 from laboratory calibrations, where the error is the ±1σ standard deviation estimated from the reproducibility of the experimental determinations. Likewise, the ratio $\alpha = \text{eCL}_{\text{CH}_3\text{O}_2}/\text{eCL}_{\text{HO}_2}$ was determined to be 65% for the measurement conditions (George et al., 2020). The values obtained from calibrations before and after the campaign agreed within their experimental errors.

Although the DUALER pressure is kept constant below the ambient pressure, variations in dynamical pressure > 10 mbar during the flight change the residence time and induce turbulences inside the inlet (Kartal et al., 2010; George et al., 2020). These may lead to different physical losses of radicals before amplification and affect the eCL. In the measurements presented in this study, variations in dynamical pressure of this magnitude were only encountered during flight level changes of the aircraft. When used during the analysis, these data sets are either excluded or flagged (P_flag). The effect of the ambient air humidity on eCL (Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003) has been accounted for by a calibration procedure reported in George et al. (2020). The [H$_2$O] in the DUALER inlet was lower than 1 × 10$^{17}$ molecules cm$^{-3}$ for 60% of measurements during EMeRGe in Europe, for which the eCL$_\text{wet} = 76\%$ of eCL$_\text{dry}$. At the highest humidity observed during the campaign, i.e., [H$_2$O]$_\text{inlet} = 2 \times 10^{17}$ molecules cm$^{-3}$, the eCL$_\text{wet}$ is 55% of eCL$_\text{dry}$ (see Fig. S1 in the supplementary information).

In addition to the measurement of RO$_2^*$ from PeRCEAS, other in-situ and remote-sensing measurements and basic aircraft data from HALO are used in this study. Details of the corresponding instruments are summarised in Table 1. The remote sensing instruments used on HALO during EMeRGe were the mini–Differential Optical Absorption (minDOAS) and the Heidelberg Airborne Imaging DOAS Instrument (HAIDI). The miniDOAS observes the atmosphere using six telescopes: two being optimised for the ultraviolet, two for the visible, and two for the near infrared. Three telescopes observe in nadir viewing and three in limb viewing. The three limb scanning telescopes point to the starboard side perpendicular to the aircraft fuselage axis. They are rotated to compensate for roll relative to the horizon. A variant of the DOAS retrieval technique uses least square fitting of the measured and radiative transfer modelled absorption along the line of sight to retrieve the differential Slant Column Density (dSCD) of the target gas and a scaling reference gas. The latter is the dimer of molecular oxygen (O$_2$). As the vertical profile of the concentrations of O$_2$ and thus O$_4$ are known then the mixing ratios of the target gas at the flight altitude is obtained from the target gas and O$_4$ dSCDs (for more details see Stutz et al., 2017; Hünke et al., 2017; Kluge et al., 2020; Rotermund et al., 2021). The HAIDI nadir observations are used to retrieve dSCDs below the aircraft. The dSCDs from HAIDI are then converted to mixing ratios using knowledge of the aircraft altitude and the corresponding geometric Air Mass Factor (AMF), calculated by a radiative transfer model under a well-mixed NO$_2$ layer assumption. As a result of this assumption, the calculated mixing ratios for HAIDI target gases are lower limits and similar to the actual values while flying within and close to a well-mixed boundary layer. In spite of the differences in sampling volume and temporal and spatial resolution between the in-situ and remote sensing measurement techniques, the concentration of the gas HCHO measured by both techniques were in good agreement and the concentrations of the NO$_2$ (remote sensing) and NO$_x$ (in situ) were consistent (for more details see Schumann, 2020).
Table 1: List of the airborne measurements and instrumentation used in this study. PeRCA: Peroxy Radical Chemical Amplification; CRDS: Cavity Ring-Down Spectroscopy; PTR-MS: Proton-Transfer-Reaction Mass Spectrometer; AT-BS: Adsorption Tube and Bag air Sampler; TD-GC-MS: Thermal Desorption Gas Chromatography and Mass Spectrometry; DOAS: Differential Optical Absorption Spectrometry; Univ: University; KIT: Karlsruher Institut für Technologie; DLR: Deutsches Zentrum für Luft- und Raumfahrt; IPA: Institut für Physik der Atmosphäre; FZ: Forschungszentrum; FX: Flugexperimente.

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4. Results and discussion

4.1. Airborne RO$_2^*$ measurements during EMeRGe in Europe

RO$_2^*$ mixing ratios up to 120 pptv were measured during the campaign, as shown in Fig. 2. Typically, the highest RO$_2^*$ mixing ratios were observed below 3000 m over Southern Europe.
Figure 2: RO$_2^*$ measured during EMeRGe-Europe: a) as a function of longitude and latitude, b) as a function of latitude and altitude.

The origin and thus the composition of the air sampled during the seven flights over Europe were different and heterogeneous. Typically, the air masses measured were influenced by emissions from MPCs and their surroundings, and sometimes by biomass burning transported over short or long distances. The concentration and mixing ratio of RO$_2^*$ rather depends on the insolation and the chemical composition of the air probed, particularly on the abundance of RO$_2^*$ precursors, than on the origin of the air masses. Since RO$_2^*$ are controlled by fast chemical and photochemical processes, the air mass origin and trajectory are not used in the calculation of RO$_2^*$ concentrations and mixing ratios but are of interest as the source of RO$_2^*$ precursors. Thus, the RO$_2^*$ variability and its production rates provide valuable insight into the photochemical activity of the air masses probed.

Changes in RO$_2^*$ as a function of latitude and altitude, as shown in Fig. 2, confirm the heterogeneity of the photochemical activity in the air masses probed. Figure 3 shows the RO$_2^*$ vertical profiles averaged for the EMeRGe flights over Europe in 500 m altitude bins. The error bars are standard errors (i.e., ± 1σ standard deviation of each bin). The vertical profiles may be biased as the higher altitudes have fewer measurements than those below 3000 m, as mentioned in section 2. The vertical profiles are a composite from averaging flights with legs carried out at different longitude and latitudes, and are only shown to summarise the variability in the composition of the air masses measured during the campaign.

Figure 3: Composite average vertical profiles of a) RO$_2^*$, b) j$_{O(1D)}$ and c) [H$_2$O] observations. The measurements are binned over 500 m altitude. The error bars are the ± 1σ standard deviation of each bin. Median values (red triangles) the interquartile 25-75% range (red-shaded area) and the number of individual measurements, n, for each bin (in green) are additionally plotted.
Most of the EMeRGe measurements below 2000 m were carried out in the outflow of MPCs, which are expected to contain significant amounts of RO$_2^+$ precursors. HALO flew at the lowest altitudes during flight legs over the English Channel, the Mediterranean, and the North Sea. The H$_2$O concentration in the air masses decreases steadily with altitude as expected. The higher relative variability in H$_2$O observed at 3000 m and the increase at 5000 m is associated with measurements under stormy conditions, often over the Alps.

4.2. RO$_2^+$ production rates

The rate of production of RO$_2^+$ from the reactions R1 to R13 is given by:

$$ \frac{d[P]}{dt} = \frac{k_2}{k_2 + k_{12}} \frac{[O_3]}{[H_2O]} + \frac{k_1}{k_1 + k_{12}} \frac{[O_3]}{[H_2O]} + \frac{[HONO]}{[HONO]} + 2[H_2O] + [O_3] + 2 \gamma [OIVO] + $$

where OIVO stands for oxygenated volatile organic compounds and $\gamma$ is the effective RO$_2^+$ yield from ozonolysis of alkenes.

In this study, Eq. 2 has been applied to the measurements taken within the EMeRGe campaign in Europe. There were no H$_2$O measurements available for EMeRGe. However, the results reported by Tan et al. (2001), indicate that the rate of OH production from the H$_2$O photolysis is not significant except when NO$_x$ is low. To be more precise, for conditions having NO < 50 ppt, the partitioning of HO$_x$ is strongly shifted to HO$_2$. HO$_2$ then predominantly reacts with itself or RO$_2$ to form peroxides, which can then photolysis. For conditions with NO > 50 pptv the rates of reactions of HO$_x$ with NO$_x$ are faster than those of HO$_2$ with HO$_2$ and RO$_2$. As the NO mixing ratio was higher than 50 pptv in 75 % of the air masses probed in Europe, the rate of the photolysis of H$_2$O$_2$ was as a first approximation assumed not to be significant source of OH for the EMeRGe dataset considered in this study.

Formaldehyde (HCHO), acetaldehyde (CH$_3$CHO), acetone, (CH$_3$C(O)CH$_3$), and glyoxal (CHOCHO) were the OVOCs measured in EMeRGe forming directly radicals through photolysis. They are produced in the photolysis and oxidation of VOCs and are likely the most abundant and reactive OVOCs present. In this study they were assumed to be the dominant VOCs in the air masses probed.

There were no measurements of alkenes provided in EMeRGe. Consequently, the ozonolysis term in Eq. 2 was not included in the analysis.

The above assumptions lead to Eq. 3, which calculates the RO$_2^+$ production rate ($P_{RO2^+}$) for the EMeRGe measurements as follows:

$$ \frac{d[P]}{dt} = 2j[O(c)] \frac{k_1}{k_1 + k_{12}} \frac{[O_3]}{[H_2O]} + \frac{[HONO]}{[HONO]} + 2[HCHO] + 2[CH_3CHO] + $$

The production rate of RO$_2^+$ molecules can be expressed in units of mixing ratio of RO$_2^+$ by dividing with the air concentration at each altitude, calculated from the pressure and temperature measurements (for the vertical profile and the latitudinal distribution of $P_{RO2^+}$ see Fig. S2 and S3 in the supplementary information). Figure 4 shows the composite averaged vertical profile of all measured RO$_2^+$ mixing ratios colour-coded with the calculated $P_{RO2^+}$. For the sake of representativeness and comparability, the number of measurements in each altitude bin is shown in Fig. 4b. The higher RO$_2^+$ mixing ratios observed below 4000 m are typically associated with $P_{RO2^+} \approx 0.4 \text{ pptv s}^{-1}$. Above 4000 m both $P_{RO2^+}$ and RO$_2^+$ start to decrease with altitude, as expected. This
is related to the decrease in H₂O and other radical precursor concentrations with altitude, as detailed in Fig. 5 and Fig. 6. In previous airborne campaigns at various parts of the world, RO₂* vertical distributions showed a local maximum between 1500 and 4000 m, as reported by Tan et al. (2001), Cantrell et al. (2003a, 2003b), and Andrés-Hernández et al. (2009). In the present work, this local maximum is more evident for measurements with P_{RO₂} ≥ 0.5 pptv s⁻¹.

Figure 4: a) Composite averaged vertical distribution of measured RO₂* colour-coded according to the value of P_{RO₂}, b) the number of measurements in each altitude bin. Small circles are 1-minute individual measurements binned with P_{RO₂} values in 0.1 pptv s⁻¹ intervals. Larger circles result from a further binning over 500 m altitude steps. All the production rates below 0.1 pptv s⁻¹ and above 0.8 pptv s⁻¹ are binned to 0.1 pptv s⁻¹ and 0.8 pptv s⁻¹, respectively. The error bars are the standard deviation for each altitude bin.

Figure 5 shows the fractional contribution of the production rate from each radical precursor reaction included in Eq. 3 as a function of altitude. The data are classified into three groups according to the rate of change of production of the RO₂* mixing ratio P_{RO₂} < 0.07 pptv s⁻¹ (5a), 0.07 < P_{RO₂} < 0.8 pptv s⁻¹ (5b), and P_{RO₂} > 0.8 pptv s⁻¹ (5c) to show the lowest, most common, and highest ranges, respectively, encountered during the campaign. For 89% of the measurements, 0.07 < P_{RO₂} < 0.8 pptv s⁻¹ applies, while the rest of the data are equally distributed in the other two P_{RO₂} ranges. The data in each group are always binned over 500 m when available.

Typically, the high amount of H₂O in the air masses probed leads to the reaction of O¹D with H₂O (reactions R1-R2a) being the highest RO₂* radical production rate (≥ 50 %) below 4000 m. As the amount of H₂O reduces with altitude, the relative contribution from O³ photolysis decreases. Above 4000 m, HCHO, HONO, and CHOCHO photolysis contributions range between 20 % to 40 %, 2.5 % to 30 %, and 5 % to 25 %, respectively. The HCHO contribution increases up to 80% during measurements above 6000 m. The contributions of CH₃CHO and CH₃C(O)CH₃ photolysis are, in contrast, practically negligible (< 5 %).
The vertical changes of the precursor mixing ratios and photolysis frequencies used to calculate $P_{RO_2}$ in Fig. 5 are shown in Fig. 6a to 6f. $P_{RO_2} < 0.07$ pptv s$^{-1}$ is associated with measurements under cloudy conditions, towards sunset where the photolysis frequencies are low, or at altitudes above 5000 m in air masses with a low amount of $RO_2^*$ precursors. $P_{RO_2} > 0.8$ pptv s$^{-1}$ are found for air masses, measured below 2000 m in the outflow of MPCs over the sea, for conditions having sufficient insolation ($j_{O(1D)} > 3 \times 10^5$ S$^{-1}$) and a high content of $RO_2^*$ precursors (HCHO $> 1000$ pptv and HONO $> 100$ pptv). The increase in the photolysis frequencies as a function of altitude is concurrent with decreases in precursor concentrations. As a result, the $P_{RO_2}$ do not significantly vary with altitude in the air masses investigated.

In previous airborne campaigns, Tan et al. (2001) and Cantrell et al. (2003b) reported a reduction of the fractional contribution of the reaction of $O(1D)$ with H$_2$O as the $P_{RO_2}$ value decreases. At very low $P_{RO_2}$ values ($< 0.03$ pptv s$^{-1}$), the sum of all other production terms exceeded the fraction from the $O(1D) + H_2O$ term. For these conditions, H$_2$O and VOCs photolysis dominated the $P_{RO_2}$. For the EMeRGe data set in Europe, only 6% of $P_{RO_2}$ are below 0.06 pptv s$^{-1}$.

![Graphs of $P_{RO_2}$ and fractional precursor contributions](image)

**Figure 5**: Total $P_{RO_2}$ and fractional precursor contributions estimated using Eq. 5 as a function of altitude, for: a) $P_{RO_2} < 0.07$ pptv s$^{-1}$, b) $0.07$ pptv s$^{-1} < P_{RO_2} < 0.8$ pptv s$^{-1}$, and c) $P_{RO_2} > 0.8$ pptv s$^{-1}$. Note the different scales in the number of measurements.
Figure 6: Vertical distribution and variation of a) to c) precursor mixing ratios; d) to f) photolysis frequencies for the P_{RO2} bins as in Fig. 5. Note the different scales in the H₂O concentration.
4.3. PSS estimation of the RO$_2^*$ mixing ratios

Under most ambient conditions in the troposphere, the RO$_2^*$ are short-lived, and the chemical lifetime of RO$_2^*$ is much shorter than the chemical transport time into and out of an air mass being probed. Consequently, pseudo-steady-state conditions prevail, and the radical production and destruction rates are balanced:

$$P_{RO_2^*} = D_{RO_2^*} \quad \text{(Eq. 4)}$$

The reactions R5 to R7, R12, R16b, and R23 to R26 are interconversion reactions between OH, RO, HO$_2$ and RO$_2$ and do consequently occur without radical losses. Solving Eq. 4 leads to Eq. 5 if RO$_2^*$ – RO$_2^*$ reactions are assumed to be the dominant radical terminating processes.

$$2j_{O_1(^{1}D)}[O_3] = \frac{k_{O_b^*+H_2O}[H_2O]}{k_{O_b^*+H_2O}[H_2O] + k_{O_b^*+O_2}[O_2] + k_{O_b^*+N_2}[N_2]} + j_{HONO}[HONO] + 2j_{HCHO}[HCHO] + 2j_{CH_2CHO}[CH_3CHO] + 2j_{CH_3C(O)CH_3}[CH_3C(O)CH_3] + 2j_{CHOCCHO}[CHOCHO] = k_{RO_2^*+RO_2^*}[RO_2^*]^2$$

where $j_{HCHO}$, $k_{CH_3CHO}$, $k_{CH_3C(O)CH_3}$, and $j_{CHOCCHO}$ are respectively $j_8$, $j_9$, $j_{10a,b}$ and $j_{11}$, as in Table 1 in the supplementary information, and $k_{RO_2^*+RO_2^*}$ represents an effective RO$_2^*$ self-reaction rate coefficient, comprising HO$_2$ – HO$_2$, HO$_2$ – RO$_2$ and RO$_2$ – RO$_2$ reaction rates.

Consequently, the RO$_2^*$ concentrations are expected to correlate with the square root of the $P_{RO_2^*}$.

Figure 7 shows the relationship between the measured [RO$_2^*$] and the calculated $\sqrt[2]{P_{RO_2^*}}$. Generally, both [RO$_2^*$] and $\sqrt[2]{P_{RO_2^*}}$ increase with the photolysis frequency of O$_3$ ($j_{O_1(^{1}D)}$). Measurements in which [RO$_2^*$] were less than $0.5 \times 10^{12}$ molecules cm$^{-3}$, $\sqrt[2]{P_{RO_2^*}}$ less than 1000 and with $j_{O_1(^{1}D)} > 5 \times 10^{-5}$ were made above 6000 m, where the amount of RO$_2^*$ precursors is low. The relatively weak correlation observed between [RO$_2^*$] and $\sqrt[2]{P_{RO_2^*}}$ indicates the necessity of other radical terminating processes and/or missing radical formation terms in the $P_{RO_2^*}$ calculation. Apart from this, the spread in the diagram confirms that the effective RO$_2^*$ self-reaction rate $k_{RO_2^*+RO_2^*}[RO_2^*]^2$ varies widely in the air masses probed likely due to the effect of changes in HO$_2$ and $\Sigma$RO$_2$ concentrations in the individual loss reaction rate coefficients. Photochemical processing is expected to be enhanced over Southern Europe due to the prevailing conditions of high insolation and temperatures during the EMeRG$e$ flights, which might lead to the rapid production of RO$_2^*$ from the photochemical oxidations of CO and VOCs. This is also reflected in the higher $P_{RO_2^*}$ and [RO$_2^*$] observed in Southern Europe as compared to those in Northern Europe (Fig. 7b).
Figure 7: Measured $[\text{RO}_2^*]$ versus calculated $\sqrt[2]{\text{P}_{\text{RO}_2^*}}$ colour-coded for values of a) $j_{\text{O}(^{1}D)}$ and b) latitude.

The correlation between $[\text{RO}_2^*]$ and $\sqrt[2]{\text{P}_{\text{RO}_2^*}}$ improves when the measurements south and north of 47°N are separately analysed (Fig. 8). For a given $[\text{RO}_2^*]$, the $\text{P}_{\text{RO}_2^*}$ calculated is higher for the measurements north of 47°N than south of 47°N. The lowest $[\text{RO}_2^*]$ to $\sqrt[2]{\text{P}_{\text{RO}_2^*}}$ ratios are associated with higher NOx (NO + NO2), especially north of 47°N, indicating the urban character and higher amounts of the RO2* precursors of the air probed (Fig. 8d). Please note that these results are only valid for the data set acquired over Europe during EMeRGe flights and do not yield a relationship between $[\text{RO}_2^*]$ and $\sqrt[2]{\text{P}_{\text{RO}_2^*}}$, which is generally applicable under all conditions for these two latitude windows.
Figure 8: Measured $[\text{RO}_2^*]$ vs $\sqrt{P_{\text{RO}_2^*}}$ for the following latitudes: a) and c) south of 47°N; b) and d) north of 47°N. Note that a) and b) are colour-coded with $J_{\text{O}(^1\text{D})}$; c) and d) are colour-coded by NO$_x$ mixing ratio. The dashed lines indicate the linear fit for visual support.

The relationship between RO$_2^*$ and $P_{\text{RO}_2^*}$ is further investigated to identify the dominant RO$_2^*$ loss process in the air masses considered in this study. As stated in section 3, HO$_2$ and RO$_2$ are not speciated but retrieved as RO$_2^*$ by the PerCEAS instrument. Because not all peroxy radicals are detected equally by the instrument, the comparison of measured and calculated RO$_2^*$ values is complicated. To investigate this the changes in the HO$_2$ to the total RO$_2^*$ ratios have been taken into consideration by $\delta$, i.e., $[\text{HO}_2] = \delta[\text{RO}_2^*]$ and $[\text{CH}_3\text{O}_2] = (1-\delta)[\text{RO}_2^*]$, in the analysis. As a first approach, RO$_2$ is assumed to consist only of CH$_3$O$_2$ to reduce the complexity of the calculations by considering only CH$_3$O$_2$ reaction rate constants. The reaction channel R25b is not considered in the calculation since the yield of this channel is < 5% (Burkholder et al., 2020) for CH$_3$O$_2$ + NO reaction. Moreover, in a previous study the ratio $\alpha = e\text{Cl}_{\text{CH}_3\text{O}_2}/e\text{Cl}_{\text{HO}_2}$ was determined to be 65% for the measurement conditions (George et al., 2020).

The Eq. 5 is additionally extended to include RO$_2^*$ effective yields from VOC oxidation and radical losses through HONO, HNO$_3$: $$ (2j_1[O_3][\beta + j_3\text{[HONO]}](1-\rho) + 2j_{10\alpha}[\text{HCHO}] + 2j_9[\text{CH}_3\text{CHO}] + 2(j_{10\alpha} + j_{10\beta})[\text{CH}_3\text{C}(\text{O})\text{CH}_3] + 2j_{11}[\text{CHOCHO}]) = \delta[\text{RO}_2^*](k_{23}[\text{NO}] + k_{24}[O_3])\rho + 2k_{15}\delta(1-\delta)[\text{RO}_2^*]^2 + 2k_{16\alpha}((1-\delta)[\text{RO}_2^*])^2 + 2k_{14}(\delta[\text{RO}_2^*])^2 \quad \text{(Eq. 6)} $$

where $\beta$ is the effective yield of OH in the reaction of O($^1\text{D}$) with H$_2$O given by:
\[ \beta = \left( \frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_3] + k_{2c}[N_2]} \right). \]

On the left-hand side of Eq. 6, 1-\( \rho \) accounts for the effective yield of HO\(_2\)+RO\(_2\) through the radical initiation reactions R2a and R3 and reactions R5 to R7 and reaction R12. As the calculation is constrained with on-board measurements, only the reactions of measured VOCs were considered in reaction R12. Similarly, on the right-hand side of Eq. 6, \( \rho \) accounts for the radical termination through the OH + NO, OH + NO\(_2\), and OH + HONO reactions (reactions R19 to R21) relative to the radical undergoing OH to peroxo radical conversion.

Consequently, \( \rho \) is given by:

\[
\rho = \frac{(k_{1a}[NO]+k_{20}[NO_2]+k_{22}[HONO])}{(k_0[O_3]+k_6[C=O]+k_7[CH_4]+k_{12a}[HCHO]+k_{12b}[CH_2CHO]+k_{12c}[CH_2C(O)CH_3]+k_{12d}[CH_3OH]+k_{12e}[CHOCHO]+k_{17}[HO_2]+k_{19}[NO]+k_{20}[NO_2]+k_{21}[HONO])}
\]

Measurements of CH\(_4\), HCHO, CH\(_3\)CHO, CHOCHO, CH\(_3\)OH, and CH\(_3\)C(O)CH\(_3\) on-board HALO are available and implemented in Eq. 6. These comprise the most abundant and reactive OVOCs and are considered to be a representative surrogate for the VOCs that act as RO\(_2\)\(^*\) precursors through oxidation and photolysis. During the EMeRGe campaign in Europe, \( k_{12a} \times \) HCHO and \( k_{12b} \times \) CH\(_3\)CHO have the highest contribution to the 1 – \( \rho \) from all the OVOC measured. Their impact on the RO\(_2\)\(^*\) budget is found to be similar because their respective concentrations compensate the difference in the rate coefficients of their reactions with OH (\( k_{12a} = 8.5 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and \( k_{12b} = 1.5 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K and 1 atm.). Despite its high mixing ratios measured, CH\(_3\)C(O)CH\(_3\) is less important in the 1 – \( \rho \) term. This is because the rate coefficient \( k(T)_{12c} \) is significantly slower than \( k_{12a} \) and \( k_{12b} \) (see Table S1 in the supplement). Similarly, the contribution of CHOCHO and CH\(_3\)OH is an order of magnitude lower than that of HCHO and CH\(_3\)CHO.

Concerning the term \( \delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])p \) on the right hand side of Eq. 6, the HO\(_2\) reaction with O\(_3\) has a negligible effect as \( k_{24} \) is almost four orders of magnitude smaller than \( k_{23} \) and the NO concentrations remained about three orders of magnitude smaller than the O\(_3\) measured during the campaign.

The impact of the methylglyoxal (CH\(_3\)C(O)C(O)H) photolysis was also investigated by using the CH\(_3\)C(O)C(O)H\(^+\) measurements provided by the miniDOAS instrument. The CH\(_3\)C(O)C(O)H\(^+\) measured is the sum of CH\(_3\)C(O)C(O)H, and a fraction of other substituted dicarbonyls (mainly 2,3-butenedione, CH\(_2\)H\(_2\)O\(_2\)), with similar visible absorption spectra. For the calculation, CH\(_3\)C(O)C(O)H was assumed to be half of CH\(_3\)C(O)C(O)H\(^+\) as recommended by Zarzana et al. (2017) and Kluge et al. (2020). The RO\(_2\)\(^*\) calculated by including CH\(_3\)C(O)C(O)H photolysis systematically overestimated the measurements. As the adequacy of the recommended factor of 0.5 varies with the actual air mass composition, CH\(_3\)C(O)C(O)H was not included in the calculations.

Figure 9 shows the fractional contribution of the destruction rate (\( D_{RO_2} \)) calculated for a 1:1 mixture of HO\(_2\) and CH\(_3\)O\(_2\) using the reactions included in Eq. 6 as a function of altitude. The data are classified into three groups according to the rate of destruction of RO\(_2\)\(^*\) mixing ratio \( D_{RO_2} < 0.01\) pptv s\(^{-1}\) (a), \( 0.01 < D_{RO_2} < 0.9\) pptv s\(^{-1}\) (b), and \( D_{RO_2} > 0.9\) pptv s\(^{-1}\) (c) to show the lowest, most common, and highest ranges, respectively, encountered during the EMeRGe campaign. For 90% of the measurements, \( 0.01 < D_{RO_2} < 0.9\) pptv s\(^{-1}\) applies, while the rest of the data are equally distributed in the other two \( D_{RO_2} \) ranges. The data in each group are always binned over 500 m when available.

As can be seen in Fig. 9, the ±1σ standard deviation of the obtained bins is very high. In spite of this, the HO\(_2\) – CH\(_3\)O\(_2\) and HO\(_2\) – HO\(_2\) reactions seem to dominate the radical destruction processes in the air masses probed. Their combined contribution is > 70
% in all the cases except in the 1000 m bin of $D_{\text{RO}_2} > 0.9$ pptv s$^{-1}$. Other significant radical losses occur through the HONO and HNO$_3$ formation. The contribution of the CH$_3$O$_2$ + CH$_3$O$_2$ reaction to the total RO$_2^*$ destruction rate is $< 5\%$.

Since Eq. 6, is quadratic in [RO$_2^*$] it can be solved for [RO$_2^*$]$_c$ where $c$ stands for calculated, as:

$$[\text{RO}_2^*]_c = \frac{-(t_{\text{RO}_2^*}) - \sqrt{L_{\text{RO}_2^*}^2 - 4(-2k_{\text{RO}_2^*})P_{\text{RO}_2^*}}}{2(-2k_{\text{RO}_2^*})}$$  \quad \text{(Eq. 7)}$$

where

$k_{\text{RO}_2^*} = (k_{16a}(1-\delta)^2 + k_{15}\delta(1-\delta) + k_{14}\delta^2)$

$L_{\text{RO}_2^*} = (\delta(k_{23}[\text{NO}] + k_{24}[\text{O}_3])p)$

$P_{\text{RO}_2^*} = (2j_1[\text{O}_3]\beta + j_3[\text{HONO}](1-\rho) + 2j_8[\text{HCHO}] + 2j_9[\text{CH}_3\text{CHO}] + 2(1.0a + j_{10a})[\text{CH}_3\text{C(O)}\text{CH}_3] + 2j_{11}[\text{CHOCHO}]]$

Figure 9: RO$_2^*$ destruction rate $D_{\text{RO}_2^*}$ and fractional contributions from loss reactions in Eq.6 as a function of altitude, for: a) $D_{\text{RO}_2^*} < 0.01$ pptv s$^{-1}$, b) 0.01 pptv s$^{-1} < D_{\text{RO}_2^*} < 0.9$ pptv s$^{-1}$, and c) $D_{\text{RO}_2^*} > 0.9$ pptv s$^{-1}$. Note the different scales in the number of measurements.

The second solution of the quadratic equation gives negative values for [RO$_2^*$]$_c$, therefore is assumed to have no physical meaning. A more detailed derivation of Eq. 6 and Eq. 7 are given in the supplementary information.
Figure 10 shows the measured RO$_2^*$ (hereinafter referred to as RO$_2^*$m) mixing ratio versus the calculated RO$_2^*$c mixing ratio using Eq. 7. RO$_2^*$m and RO$_2^*$c are the measured and calculated RO$_2^*$ respectively for $\delta = 1$, i.e., RO$_2^*$ = HO$_2$ and $\delta = 0.5$, i.e., HO$_2$ = RO$_2$.

The eCL corresponding to $\delta = 1$ and $\delta = 0.5$ used for the RO$_2^*$m retrievals were determined in laboratory experiments, as reported by George et al. (2020). The small circles represent 1-minute RO$_2^*$m, whereas the large circles are the mean of the RO$_2^*$m binned over 10 pptv RO$_2^*$c intervals. The RO$_2^*$ data are colour-coded with the on-board NO measurements. The linear regression slopes are around 0.7 ($R^2 = 0.96$), indicating an overall 25 − 30 % overestimation of the RO$_2^*$m. The y-axis intercept is below the instrumental detection limit for most measurement conditions. Table 2: Linear regression parameters from RO$_2^*$m versus RO$_2^*$c using Eq.7 from Fig.10.

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Figure 10: RO$_2^*$m versus RO$_2^*$c using Eq. 7 for a) $\delta = 1$ and b) $\delta = 0.5$. The data are colour-coded with the measured NO mixing ratios. The 1-minute (small circles), the mean of the binned RO$_2^*$m over 10 pptv RO$_2^*$c intervals (large circles), and the median of each bin (grey triangles) are shown. The error bars indicate ± 1σ standard deviation of each bin. The linear regression for the binned values (solid line) and the 1:1 relation (dashed line) are also depicted for reference.

Figure 11 shows the vertical profiles of RO$_2^*$m and RO$_2^*$c mixing ratios calculated for $\delta = 0.5$, averaged for the EMeRGe flights over Europe in 500 m altitude bins. RO$_2^*$c seems to overestimate RO$_2^*$m for altitudes above 4000 m. As mentioned in Sect. 4.1, the vertical profiles are a composite from averaging flights with legs carried out at different longitude and latitudes. Therefore, the differences between RO$_2^*$m and RO$_2^*$c have been studied in more detail respect to the composition of the individual air masses (see the RO$_2^*$m and RO$_2^*$c mixing ratios as a function of latitude and altitude in Fig. S4 in the supplementary information).
Figure 11: Vertical distribution of the mean RO$_2^*$$_m$ and mean RO$_2^*$$_c$ using Eq. 7 for $\delta = 0.5$ for the EMeRGe data set in Europe. The measurements are binned over 500 m altitude. The error bars are the ± 1σ standard deviation of each bin. Median values (red and green triangles) the interquartile 25-75% range (red and blue shaded areas) and the number of individual measurements, n, for each bin (in green) are additionally plotted.

Figure 12 shows the data for $\delta = 0.5$ colour-coded with NO, NO$_x$, the sum of HCHO, CH$_2$CHO, CHOCHO, CH$_3$OH, and CH$_3$(C(O)CH$_3$ (from now on referred to as $\Sigma$VOCs), as a surrogate for the amount of OVOCs acting as RO$_2^*$ precursors, and the $\Sigma$VOCs to NO ratio. The largest differences between RO$_2^*$$_m$ and RO$_2^*$$_c$ are observed for the bins around 50 pptv. The RO$_2^*$$_c$ overestimate the RO$_2^*$$_m$ mostly for RO$_2^*$$_m$ < 25 pptv observed above ≈ 4000 m. These air masses are characterised by NO < 50 pptv, $\Sigma$VOCs typically below 4 ppbv, high $\Sigma$VOCs/NO ratios (> 50), and low insolation conditions, i.e., $J_{O(\Delta)}$ < 2 × 10$^{-5}$ s$^{-1}$ (see Fig. S5 in the supplementary information). Under these insolation conditions, the radical production rate is expected to be low, and the RO$_2^*$ − RO$_2^*$ reactions are expected to dominate the RO$_2^*$ loss processes. As OH and H$_2$O$_2$ were not measured during the EMeRGe campaign in Europe, Eq. 7 does not include the loss reactions R17 and R18, which might be significant under such conditions (Tan et al., 2001) and explain the overestimation of RO$_2^*$$_m$. This is also the case for the overestimations observed below 40 pptv RO$_2^*$$_m$ at other altitudes, where NO < 50 pptv but the $\Sigma$VOCs/NO ratios remain low. The overestimation may therefore be independent of the $\Sigma$VOCs/NO ratios. For NO ≤ 50 pptv, NO$_2$ ≤ 100 pptv, RO$_2^*$ ≤ 40 pptv and HCHO ≤ 1 ppbv, the rate of reaction R17, which forms H$_2$O and O$_2$ from OH and HO$_2$, is about 4 times faster than the rate of the OH oxidation reaction of the dominant OVOCs (reaction R12) considered in this study or the rate of formation of HONO (reaction R19).
RO$_2^{*}_m$ is both underestimated and overestimated for ∑VOCs mixing ratios greater than 7 ppbv. The composition of these air masses is very different, as reflected by the ∑VOCs/NO ratios. This implies that Eq. 7 does not capture the peroxy radical yields adequately from the measured VOCs and OVOC in these cases. The differences between RO$_2^{*}_m$ and RO$_2^{*}_c$ may be explained in part by a) changes in OH yields due to additional VOC oxidation processes, which are not in Eq. 7 and/or b) RO$_2^{*}$ production from the photolysis of carbonyls, which were not measured and/or c) RO$_2^{*}$ production from the ozonolysis of alkenes or unidentified biogenic terpene emissions and/or d) overestimation of the loss processes.

In addition, Eq. 7 does not consider the loss of RO$_2$ through the organic nitrate formation (reaction R25b) which results in an underestimation of radical loss in the presence of RO$_2$ with higher organic group. Tan et al., 2019 reported changing the yields for organic nitrate formation channel in reaction R25 from 5% to 20% has a small but notable influence on their experimental budget analysis. Similarly, the RO$_2$ loss through organic nitrate formation which are not included in Eq. 7 might explain the RO$_2^{*}_m$ overestimations for ∑VOC < 2ppb and ∑VOCs/NO < 20, and for NO > 200 pptv.

Figure 12: RO$_2^{*}_m$ versus RO$_2^{*}_c$ using Eq. 7 for δ = 0.5 colour-coded with the measured a) NO mixing ratio, b) NO$_x$ mixing ratio, c) ∑VOCs mixing ratio, where ∑VOCs = HCHO + CH$_3$CHO + (CHO)$_2$ + CH$_3$OH + CH$_3$C(O)CH$_3$, and d) ∑VOCs/NO ratio. The 1-minute (small circles), the mean of the binned RO$_2^{*}_m$ over 10 pptv RO$_2^{*}_c$ intervals (large circles), and the median of each bin (triangles) are shown. The error bars represent the ± 1σ standard deviation of each bin. The linear regression for the binned values (solid line) and the 1:1 relationship (dashed line) are plotted for reference.
Although considered small, the spatial and temporal differences in the in-situ measurements of the key trace gases (O$_3$, NO, H$_2$O, CO, CH$_4$, VOCs) as compared to those of the remote sensing observations (NO$_2$ and HONO) used in Eq. 7 may also contribute to the overall spread observed in Fig. 12. Although the temporal evolution and the amount of the trace gases measured using in-situ and remote sensing instruments agree reasonably well, as shown for HCHO in Fig. 13, the remote sensing instruments have, in general, larger air sampling volumes compared to that of in-situ instruments. This may occasionally lead to significant differences depending on the location of the pollutant layers with respect to HALO. In addition, PTR-MS measurements of HCHO might include interferences from molecular fragments of other compounds in the sample air (Inomata et al., 2008). Further details about the accuracy and comparability of the instrumentation on-board during the campaign can be found elsewhere (Schumann, 2020).

![Figure 13: An example of the time series of the measured HCHO mixing ratios retrieved from the remote sensing (HAIDI in blue and miniDOAS in green) and in-situ (HKMS in red) instruments during the E-EU-04 flight on 14.07.2017. The shaded region shows ± 1σ uncertainties of the HKMS and miniDOAS instruments. The flight altitude is depicted in black.](image)

In summary, apart from the inaccuracies in the reaction rate coefficients, the differences between RO$_2^*$$_m$ and RO$_2^*$$_c$ might be caused by a combined effect of the limitations of the analytical expression to simulate complex non-linear chemistry and the measurement uncertainties arising from the spatial heterogeneity of the plume for the remote sensing instruments. Consequently, the quantification of limiting factors in Eq. 7 require the analysis of the pollution events encountered along the flights individually.

The ratio of RO$_2^*$$_m$ to RO$_2^*$$_c$ (RO$_2^*$$_m$/RO$_2^*$$_c$) has been used to assess the applicability of Eq. 7 for the calculation of RO$_2^*$ in the air masses probed. In Fig. 14, the data are colour-coded with respect to RO$_2^*$$_m$/RO$_2^*$$_c$, H$_2$O, ΣVOCs, and NO$_x$. The air masses probed at altitudes above 2000 m are close to the PSS assumptions used to develop Eq. 7, and consequently, the RO$_2^*$$_m$/RO$_2^*$$_c$ remains ≤ 1. In contrast, RO$_2^*$$_m$/RO$_2^*$$_c$ is at its highest value below 2000 m, reaching up to 3. At these altitudes, most of the flights in Europe were carried out in pollution plumes, in which both the amount of NO$_x$ and RO$_2^*$ precursors are high. The analytical expression does not capture the RO$_2^*$ variations resulting from fast non-linear photochemistry present in these pollution plumes. This is the case for the measurements made between 42°N and 46°N in the outflow of Po Valley and Rome. ΣVOCs > 7 ppbv and NO$_x$ mixing ratios > 500 pptv indicate high radical precursor loading and relatively fresh emissions. The RO$_2^*$$_m$/RO$_2^*$$_c$ is also > 2 in the measurements over the English Channel (between 50°N and 52°N) with ΣVOCs and NO$_x$ mixing ratio > 7 ppbv and 1000 pptv, respectively.
The applicability of Eq. 7 for calculating the in-flight measurements of RO₂⁺ along the track of the E-EU-03 flight on 11 July 2017 was studied in more detail. The E-EU-03 flight investigated the outflow of selected MPCs in Italy (i.e., Po Valley and Rome). Consequently, the flight track was routed along the western coast of Italy and included vertical profiling over the Tyrrhenian Sea upwind of Rome (see Fig. S6 in the supplementary information). As indicated by the O(1D) in Fig. 15, cloudless conditions dominated throughout the flight track. The RO₂⁺ agree reasonably well with RO₂⁺ measured throughout this period except in the pollution plume measured from 12:05 to 12:25 UTC. In this plume, CO, NO, NO₂, HONO, NOₓ, and HCHO were 100 ppbv, 180 pptv, 150 pptv, 120 pptv, 1 ppbv and 2 ppbv, respectively. The RO₂⁺ are approximately 20% underestimated by RO₂⁺ during this period. Backward trajectories calculated using FLEXTRA indicate the transport of pollution through the Mediterranean mixed with dust plumes originating from Tunisia. The NO mixing ratios observed indicate the proximity to emission sources.

The measurements of VOCs used in Eq. 7 may not be representative of the actual complex VOC composition in the plume measured from 12:05 to 12:25 UTC. Consequently, the RO₂ to HO₂ ratio, the branching ratios and effective rate coefficients for RO₂⁺ – RO₂⁺ reactions might not be well represented in Eq. 7. Taking CH₃O₂ as a surrogate for all RO₂ might lead to uncertainties.
in the RO$_2^*$ calculations in the presence of OVOCs with larger organic chains. On the experimental side, changes in the HO$_2$ to RO$_2$ ratio affect the accuracy of the PeRCEAS retrieval of the total sum of radicals. As noted in section 3, in this study RO$_2^*$ = HO$_2$ + 0.65 × RO$_2$, and the eCL is determined for a 1:1 mixture of HO$_2$:CH$_3$O$_2$, i.e. $\delta = 0.5$ is used for the RO$_2^*$ retrieval. However, the HO$_2$ to CH$_3$O$_2$ ratio is not expected to remain constant in all the air masses probed. For a 3:1 ratio of HO$_2$:RO$_2$, the RO$_2^*$ would decrease by 10%. Similarly, a HO$_2$:RO$_2$ ratio of 1:3 would lead to an increase of 10% in the reported RO$_2^*$.

This uncertainty is well below the in-flight uncertainty of the PeRCEAS instrument indicated by the error bars in Fig. 14 (George et al., 2020), and cannot account for the overall underestimation. However, it might reduce the differences observed between RO$_2^*_{m}$ and RO$_2^*_{c}$ in particular cases. A complete explanation of the variability of RO$_2^*$ in the pollution plumes measured within the campaign in Europe is beyond the scope of this analysis and requires an investigation by high-resolution chemical models.

Figure 15: Temporal variation of RO$_2^*_{m}$ and RO$_2^*_{c}$, selected radical precursors and $j_{O(1D)}$ along the E-EU-03 flight track: a) RO$_2^*_{m}$, RO$_2^*_{c}$ mixing ratios. The flight altitude is indicated in black. The $P_{\text{flag}}$ indicates RO$_2^*$ measurements affected by dynamical pressure variation in the inlet; b) O$_3$, CO, HCHO mixing ratios, and $j_{O(1D)}$; c) NO, NO$_2$, NO$_y$, and HONO mixing ratios.
4.4. Comparison of results with other studies

4.4.1 RO$_2^*$ production rate

Cantrell et al. (2003b) proposed that the production of RO$_2^*$, $P_{RO_2^*}$, is equal to the sum of two terms representing RO$_2^*$ – RO$_2^*$ reactions and the RO$_2^*$ – NO$_x$ reactions in the troposphere. As a result of this assumption, these authors describe the relationship between HO$_2$, RO$_2$, $P_{RO_2^*}$ and NO$_x$ as:

$$P_{RO_2^*} = k_{RR} [HO_2 + RO_2]^2 + k_{RN} [HO_2 + RO_2] [NO_x]$$  \hspace{1cm} (Eq. 9)

where $k_{RR}$ and $k_{RN}$ refer to effective rate coefficients for RO$_2^*$ – RO$_2^*$ and RO$_2^*$ – NO$_x$ reactions, and are calculated as fit parameters. Solving Eq. 9 for $[HO_2 + RO_2]^2$ leads to:

$$[HO_2 + RO_2] = \sqrt[2]{A} + B^2 - B$$  \hspace{1cm} (Eq. 10)

where $A = \frac{P_{RO_2^*}}{k_{RR}}$ and $B = \frac{k_{RN}[NO_x]}{2k_{RR}}$. For low NO$_x$ and/or high $P_{RO_2^*}$, B becomes negligible compared to A. Then $[HO_2 + RO_2]$ approaches $\sqrt[2]{A}$ and is independent of NO$_x$. For high NO$_x$ and/or low $P_{RO_2^*}$, $[HO_2 + RO_2]$ approaches zero.

The RO$_2^*$ and RO$_2^*$ for the EMeRGe observations in Europe, binned in 0.1 pptv s$^{-1}$ $P_{RO_2^*}$ intervals, were fitted according to the procedure of Cantrel et al. (2003b) and the results are shown in Fig. 16. The obtained fit parameters for Fig. 16a and Fig. 16b are $k_{RR} = 7 \times 10^{-5}$, $k_{RN} = 9 \times 10^{-6}$. The RO$_2^*$ calculated by Eq. 7 appears to be close to the linear function of the NO$_x$ measured. Similar to the results of the study of Cantrell et al. (2003b), a decrease of RO$_2^*$ with NO$_x$ is identified for NO$_x > 1000$ pptv. RO$_2^*$ does not show the decrease with increase in NO$_x$ for $P_{RO_2^*} > 0.7$ pptv s$^{-1}$. This might be explained by the under estimation of radical losses through organic nitrate formation in Eq. 7 as explained in section 4.3.

Despite the low agreement of the fitted lines with the RO$_2^*$, a decrease of the RO$_2^*$ as a function of NO$_x$ is still observed. The disagreement between the RO$_2^*$ and the curves estimated using Eq. 10 implies that the simplified Eq. 9 from Cantrell et al. (2003b), is insufficient to adequately describe the chemical and physical processes occurring in the air masses probed. Part of the disagreement might arise from missing terms in the $P_{RO_2^*}$ calculated using Eq. 3 or inaccuracies related to the NO to NO$_2$ ratio in the air mass, which are more evident at higher $P_{RO_2^*}$. As expected, the ratio of calculated [RO$_2^*$] to $\sqrt[2]{P_{RO_2^*}}$ has a negative linear dependence on the measured [NO$_x$] (see Fig. 16a). The comparable relationship of $\frac{RO_2^*}{\sqrt[2]{P_{RO_2^*}}}$ to [NO$_x$] is not linear for NO$_x < 100$ pptv approximately (see Fig. 16d). This indicates that the simplified approach of Cantrell et al. (2003b) is not applicable to the more complex non-linear processes involved in the air masses investigated within EMeRGe.
Figure 16: a) \( \text{RO}_2^* \) binned into \( P_{\text{RO}_2} \) intervals of 0.1 pptv s\(^{-1}\) versus binned \( \text{NO}_x \); b) \( \text{RO}_2^* \) \( m \) binned into \( P_{\text{RO}_2} \) intervals of 0.1 pptv s\(^{-1}\) versus binned \( \text{NO}_x \); c) ratio of \( \left[ \text{RO}_2^* \right]_c \) to \( \sqrt{P_{\text{RO}_2}} \) versus \( \text{NO}_x \); and d) \( \left[ \text{RO}_2^* \right]_m \) to \( \sqrt{P_{\text{RO}_2}} \) ratio versus \( \text{NO}_x \). The data in the a) and b) panels are assigned different colours, as a function of the radical production rate interval. The \( \text{NO}_x \) observations are binned into 50 equidistant intervals on a logarithmic scale. The solid lines in panels a) and b) are the least square fits, obtained using Eq. 9. In panels c) and d) the ratio of \( \left[ \text{RO}_2^* \right]_c \) to \( \sqrt{P_{\text{RO}_2}} \) and \( \left[ \text{RO}_2^* \right]_m \) to \( \sqrt{P_{\text{RO}_2}} \) are binned into 50 \( \text{NO}_x \) intervals equidistant on the logarithmic scale from 10 to 10000 pptv. Error bars indicate the ±1σ standard deviation for the distribution in each bin.

4.4.2 \( \text{O}_3 \) production rate

The \( \text{O}_3 \) production rate \( (P_{\text{O}_3}) \) is calculated from the EMERGe Europe dataset using the reaction of \( \text{RO}_2^* \) with \( \text{NO} \) in a similar manner to that used in previous studies of photochemical processes in urban environments (e.g. Kleinman et al., 1995; Volz-Thomas et al., 2003; Mihelcic et al., 2003; Cantrell et al., 2003b; and references herein).

\[
P_{\text{O}_3} = k_{\text{RO}_2^*+\text{NO}} \left[ \text{RO}_2^* \right][\text{NO}] \quad \text{(Eq. 11)}
\]

where \( k_{\text{RO}_2^*+\text{NO}} \) is taken as the average of \( k_{\text{HO}_2+\text{NO}} \) and \( k_{\text{CH}_3\text{O}_2+\text{NO}} \).

Figure 17 shows the mean \( P_{\text{O}_3} \) calculated using Eq. 11 from the \( \text{RO}_2^* \) \( m \) and \( \text{RO}_2^* \) \( c \) as a function of \( \text{NO} \). The measurements are binned into 50 \( \text{NO} \) mixing ratio bins. The bin size increases with \( \text{NO} \) to keep the points equidistant on the logarithmic scale. The calculated \( P_{\text{O}_3} \) for the \( \text{RO}_2^* \) \( m \) and \( \text{RO}_2^* \) \( c \) agree well within the standard deviation of the bins.
Figure 17: Calculated O$_3$ production rate (P$_{O_3}$) determined using RO$_2^\star_m$ (red dots) and RO$_2^\star_c$ (blue dots) as a function of: a) NO mixing ratio; b) NO number density. The 1-minute measurements are binned into 50 bins of NO equidistant on the logarithmic scale for panel a) from 10 to 10000 pptv and for panel b) from 5 × 10$^7$ to 3.5 × 10$^{10}$ molecules cm$^{-3}$ respectively. The shaded area shows the ± 1σ standard deviation of each bin. To facilitate comparison with ground-based measurements, the black line plotted in panel b) is the number density corresponding to 1 ppbv NO at 1000 mbar and 25°C.

Similar P$_{O_3}$ values have been reported for ground-based measurements in polluted areas such as Wangdu (Tan et al., 2017) and Beijing (Whalley et al., 2021) and similar ranges of peroxy radicals and NO mixing ratios. In previous work, Whalley et al. (2018) calculated P$_{O_3}$ to be about an order of magnitude lower than that found in this study from observations in central London for about an order of magnitude lower amount of HO$_2$ + RO$_2$. For NO > 1 ppbv, the P$_{O_3}$ estimated from the measurement of HO$_2$ and RO$_2$, or from the assumptions of an HO$_2$ to RO$_2$ ratio were underestimated by the models in other studies in the urban atmosphere (e.g. Martinez et al., 2003; Ren et al., 2003; Kanaya et al., 2008; Mao et al., 2010; Kanaya et al., 2012; Ren et al., 2013; Brune et al., 2016; Griffith et al., 2016). This behaviour is generally attributed to an underestimate of large RO$_2$ concentrations, which likely undergo multiple bimolecular reactions with NO before forming an HO$_2$ radical.

During the EMeRGe campaign in Europe, the NO mixing ratios were < 1 ppbv (approximately < 3 × 10$^{10}$ molecules cm$^{-3}$). The ozone production rates obtained for both RO$_2^\star_m$ and RO$_2^\star_c$ are in reasonable agreement with other modelling studies in urban environments where the mixing ratio of NO is < 1 ppbv (Tan et al., 2017; Whalley et al., 2021).

5. Summary and conclusions

This study exploits the airborne measurements of various atmospheric constituents on-board the HALO research aircraft over Europe in summer 2017 to investigate radical photochemistry in the probed airmasses. RO$_2^\star$ are calculated by assuming a photostationary steady-state (PSS) of RO$_2^\star$ and compared with the actual measurements. The calculation is constrained by the simultaneous airborne measurements of radical precursors, photolysis frequencies and reactants of RO$_2^\star$ such as NO$_x$ and O$_3$. The calculated radical production rates P$_{RO_2}$ do not significantly vary with altitude in the air masses investigated as the increase in the photolysis frequencies as a function of altitude is concurrent with decreases in precursor concentrations.
The significance and the importance of selected initiating and terminating processes in the RO$_2^*$ chemistry are investigated by gradually increasing the complexity of the analytical expression. The agreement of the calculations with the measurements over a wide range of chemical composition and insolation conditions improves when the analytical expression is extended to account for effective radical yields from VOC oxidation and radical losses through nitrates and nitrites formation. The RO$_2^*$ measured is usually overestimated when NO is < 50 pptv in the air probed. This behavior might be explained by RO$_2^*$ loss processes involving reactions with OH (e.g., the reaction of HO$_2$ with OH, but possibly to a lesser extent the three-body reaction of OH with itself to make H$_2$O$_2$). These reactions may become significant RO$_2^*$ loss processes at low NO concentrations as measured during the campaign but are excluded from the analytical expression, which is constrained by on-board measurements. Similarly, the RO$_2$ loss through organic nitrate are also excluded from the analytical expression. These reactions may become significant RO$_2^*$ loss processes in the presence of RO$_2$ with higher organic groups. This might explain some of the RO$_2^*$ overestimations by the analytical expression observed for NO > 200 pptv.

The RO$_2^*$ calculated under assumption of a photostationary state mostly underestimated the RO$_2^*$ measured in polluted plumes of urban origin at altitudes below 2000 m. Changes in the HO$_2$ to RO$_2$ ratios in different plumes can account for the disagreement in particular cases. In pollution plumes with the sum of the OVOCs measured mixing ratios being higher than 7 ppbv approximately, the underestimation of the measurements can reach up to 80%. In these plumes, the oxidation and/or photolysis of VOCs, which were not measured, and the ozonolysis of alkenes might be significant sources of RO$_2^*$, limiting the accuracy of the analytical expression. More information about peroxy radical speciation and VOC partitioning is required to better describe the fast photochemistry in these pollution plumes.

However, the analytical expression developed is robust enough to simulate the radical chemistry in most of the conditions in the free troposphere encountered during EMeRGe in Europe. Speciated radical and VOC measurements in future campaigns would facilitate the estimation of radical loss reactions in air masses having NO < 50 pptv and improve radical production rates estimations in pollution plumes having a high amount of VOCs, where non-linear complex chemistry is involved. Comparing RO$_2^*$ measurements with RO$_2^*$ calculations from the analytical expression helps to identify different chemical and physical regimes, which can be used to constrain future model studies.

The calculated O$_3$ production rates for NO < 1 ppbv are in the same order of magnitude as those previously reported for urban environments. This indicates that the selected RO$_2^*$ production and loss processes and observations of the radical precursors onboard are, to a good approximation, adequate for the estimation of the O$_3$ production in the measured airmasses in the free troposphere over Europe.

Disclaimer. Competing interests. The authors declare that they have no conflict of interest.

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Author contribution:
MG, VN, and YL undertook the RO\textsuperscript{2}\textsuperscript{+} measurements, flying as key scientists on-board HALO. VN led the deployment of PeRCEAS in the HALO aircraft. MG led the analysis of the PeCEAS measurements and prepared the manuscript with contributions from all co-authors. MDAH and JPB initiated the EMeRGe research project and consortium, acted as co-principal and principal investigators, and participated in the measurement campaigns. They developed the overarching EMeRGe scientific objectives and the required measurement portfolio, directed the EMeRGe research campaigns, and participated in the data analysis presented. AZ, BB, BS, EF, FO, FK, HS, HZ, KB, KP, and TH have contributed by providing their measurements made on-board HALO during the campaign and participated in the discussion of results.

**Competing interests:**

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