Peroxy Radical Measurements from R/V Brown During TexAQS 2006

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Introduction

- Peroxy radicals are key intermediates of the oxidation of Volatile Organic Compounds (VOCs) in the troposphere.
- They are formed from the initial reaction of VOCs with OH, NO, Cl, or O3, followed by reaction with O2.
- Peroxy radicals are central to the formation of ozone, because they oxidize NO to NO2 (Eq. 1), whose photolysis is the only known source of ozone (Eq. 2). Ozone is destroyed instantly by photolysis (Eq. 2). Ozone is destroyed instantly by photolysis (Eq. 2). Ozone is destroyed instantly by photolysis (Eq. 2). Ozone is destroyed instantly by photolysis (Eq. 2).
- The instrument deployed on the R/V Brown in the TexAQS-GoMACCS 2006 campaign using a Chemical Amplification technique.
- Together with OH, NO, NO2 photolysis rates and the other chemical and physical parameters measured during the campaign, the measurements were used to estimate the Net Photochemical Ozone Production (NPO) in Southern Texas and to study radical chemistry in the lower troposphere.

PERoxy Radical Chemical Amplifier (PERCA)

- The instrument deployed on the R/V Brown (Fig. 1, left) was a dual-channel PERCA (PERoxy Radical Chemical Amplifier) designed at the University of East Anglia (UK) and built at the University of Leicester (UK) (Chen et al., 2006).
- The Chemical Amplification technique (Cantrell et al., 1984) is based on the radical-catalyzed conversion of NO and CO into NO2 and CO2. The yield of NO2 and CO2 is equal to k1/2 [O3] + [RO2] + [NO][NO2] + [CO][CO2], where k1 is the chain length, i.e., the number of OH-RO2 inter-conversion cycles that occur before removal of radicals from the system by heterogeneous loss on the walls and/or formation of HONO, EMNO, and NO3/NO2 (Fig. 1, right).

Total Peroxy Radicals Concentrations

- The dual channel of HO2/RO2 measured at different locations during TexAQS-GoMACCS 2006 are shown in Fig. 2.
- On average, the measured concentration of HO2+RO2 was 20–40 ppt in the middle of the day and 10–20 ppt during the night. The comparatively little difference between day and night is likely due to the day-time suppression of peroxy radicals by high [NO2] during most of the cruise.
- The highest concentration during the cruise was 108 ppt, measured on September 7 at Jacinto Point at 9:15 GMT (13:15 LT). The daytime maximum was 166 ppt and was measured on September 7 in the Houston Ship Channel at 20:35 GMT (15:35 LT).

Net Photochemical Ozone Production

- The Net Photochemical Ozone Production is the difference of the in-situ O3 production and loss rates.
- Assuming that only peroxy radicals oxidize NO to NO2 and that ozone is destroyed only by photolysis and reactions with OH and NO2, the Net Photochemical Ozone Production (NPO) is

\[ NPO = \frac{d}{dt}[NO] = \frac{k_1}{2} [O3] + [RO2] + [NO][NO2] + [CO][CO2]. \]

- OH was estimated using measured NO2, [RO2] and [NO] and NO2 was assumed to be a fraction of measured HO2+RO2. A generic rate coefficient (\(k_2\)) was used for the reaction of RO2 with NO2 to form \(3 \times 10^{-15} \) molecules on \(1 \) s

- Sensitivity tests showed that [NO2] is relatively insensitive to the value of \(k_2\), but 2–3% to the concentration of OH (4–5 ppt) and to the HO2/RO2 ratio (7–10%).

Case Studies

- Fig. 4 shows three case studies of radical chemistry: a change of chemical regime from polluted to clean, an example of night-time chemistry and an high ozone event.
- On 10 August (Fig. 4, left) the ship was on the Sabine River, leaving the industrial area of Beaumont towards the Gulf. A storm occurred in the early afternoon stopping photochemical production of radicals. After the storm, radicals increased again due to ozone photolysis. The ship was by now in the Gulf, far from emission sources, and the concentration of radicals was about half than before the storm, with much lower levels of HCHO.

Summary and Future Work

- Measurements of total peroxy radicals (RO2+HO2) were made on board the R/V Brown during the TexAQS-GoMACCS 2006 campaign using a Chemical Amplification technique.
- The measurements were used to identify case studies of radical chemistry and to estimate the Net Photochemical Ozone Production at different locations. Values of NPO ranged from -10 to 40 ppt in the Gulf up to 200 ppt/h in the Houston Ship Channel.
- The measurements of HO2/RO2 need to be corrected for temperature and humidity.
- Data analysis to come: the Photochemical Ozone Production can be estimated from the Photostationary State (PSS) and compared with the one calculated from the total peroxy radicals measurements.
- A box-model based on the MCM and constrained to the measurements will be built and used to model the concentrations of radicals (RO2+HO2) and NO3 for comparison with the measurements, to estimate the concentration of O3, which was not measured during the campaign, and to study the details of the radical chemistry under the conditions encountered during the R/V Brown cruise.

Acknowledgements


References


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Figure 1: Measurements on the R/V Brown (left). Scheme of the Chemical Amplification technique (right).

Figure 2: Total Peroxy Radicals Concentrations

Figure 3: Net Photochemical Ozone Production

Figure 4: Case Studies

Figure 5: Summary and Future Work

Acknowledgements
