

PRICE II

Peroxy
Radical
Inter
Comparison
Exercise

PRICE 2 was a formal laboratory intercomparison of techniques to measure atmospheric concentrations of peroxy radicals (HO_2 and RO_2), including the procedures used for calibration of the chemical amplifiers

Highlights from PRICE 2

- The HO_2 calibration sources used by several groups agreed within 10%
- The sensitivity of the chemical amplifier has a strong water dependence. If not accounted for, atmospheric RO_2 concentrations are underestimated by a factor of 2-4. (*Mihele and Hastie GRL, 1997, Mihele et al., IJCK, 1997*)
- The chemical amplifier responds to ClO_x radicals with twice the sensitivity as for HO_2 . (*Arnold, Ph.D. Thesis, 1997, Martinez et al., 1999*)

For more information, read the executive summary, view our list of publications or write an email to a.volz-thomas@fz-juelich.de.

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Peroxy Radical Chemistry

Peroxy radicals (HO_2 and its organic homologues RO_2) are important intermediates in atmospheric photo-oxidant formation. They arise from the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) by hydroxyl radicals (OH), nitrate radicals (NO_3), halogen atoms and ozone (O_3). Depending on the prevailing NO concentration, ozone and other photo-oxidants, e.g. peroxides, PAN and other organic nitrates, are formed in this mechanism. While atmospheric measurements of OH are essential for establishing the accuracy of the basic theories about atmospheric photochemistry, measurements of RO_2 and HO_2 provide a deeper insight into the mechanism of photooxidant formation, as their concentrations are sensitive to both the chemical composition and actinic fluxes experienced by an air parcel.

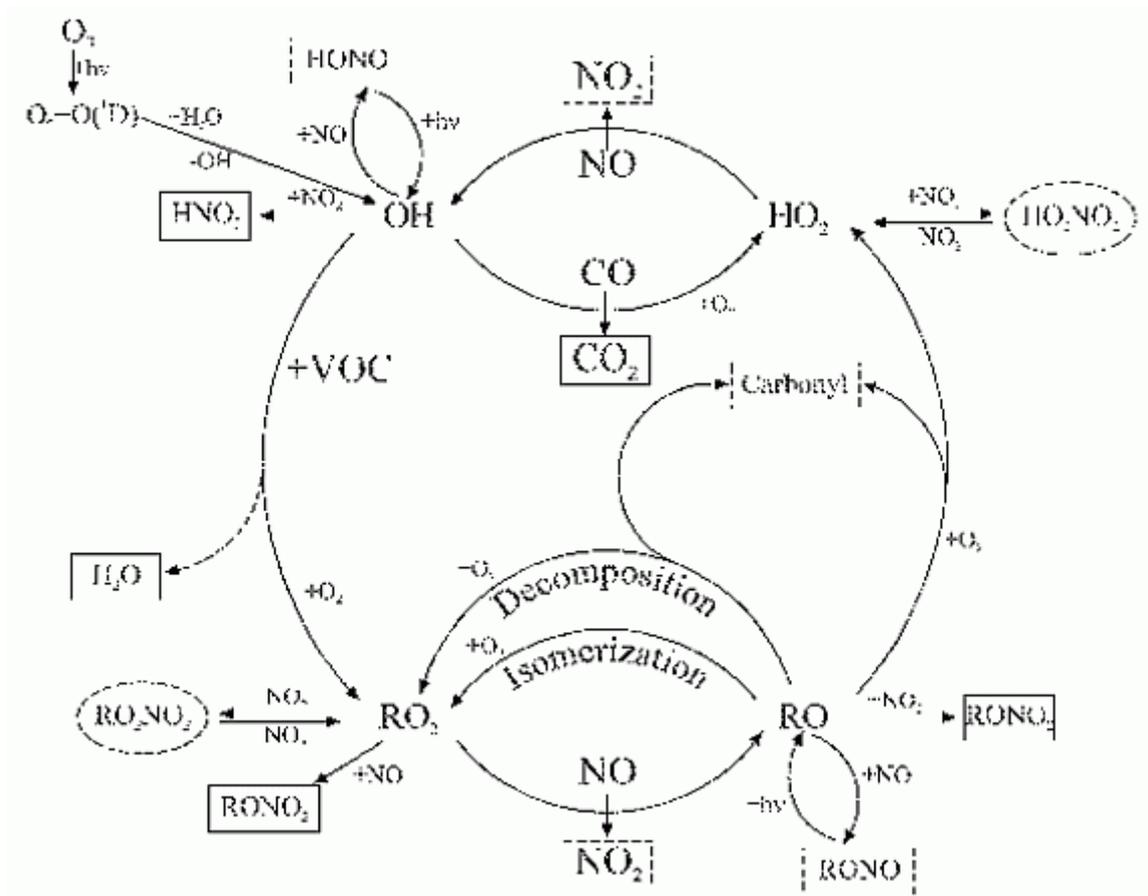
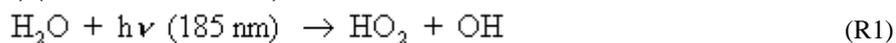


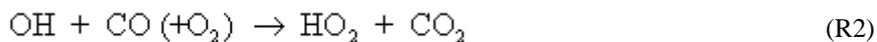
Figure 1 summarizes the most important radical reactions at high NO_x concentrations.

The HO_2 calibration source

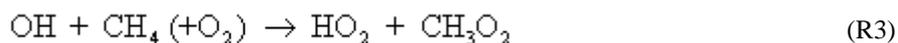
The HO_2 calibration source relies on the photolysis of H_2O by the 185 nm -Hg-line which generates equal amounts of HO_2 and OH (R1) (Schultz *et al.*, 1995).



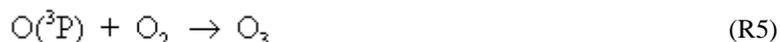
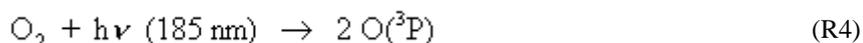
Addition of sufficient CO (several 100 ppm) is used to convert OH into HO_2 (R2). Then, two HO_2 molecules are produced upon absorption of one photon.



By replacing the CO with a hydrocarbon, a mixture of 50% RO_2 and 50% HO_2 is generated (e.g. R3), provided that photolysis of the precursor hydrocarbon (or impurities) can be neglected.



The actinic flux of the low-pressure Hg-lamp in the 185 nm line is measured in-situ using O_2 photolysis at 185 nm which produces 2 O_3 molecules (R4 and 2x R5).



When CO is used to convert OH into HO₂, the HO₂ concentration directly after the illumination zone can be determined from the measured concentrations of H₂O, O₂ and O₃, the [absorption cross sections of oxygen and water at 185 nm](#) and the quantum yields for R1 and R4. Potential losses of the radicals between the photolysis region and the point of measurement need to be quantified by profiling measurements and/or the real source output needs to be verified with an independent, absolute method. The HO₂ concentration is therefore calculated according to equation (1)

$$[\text{HO}_2] = \eta \cdot \frac{[\text{H}_2\text{O}] \cdot \sigma_{\text{H}_2\text{O}} \cdot 2 \cdot \Phi_{\text{R1}}}{[\text{O}_2] \cdot \sigma_{\text{O}_2} \cdot \Phi_{\text{R4}}} \cdot [\text{O}_3] \quad (1)$$

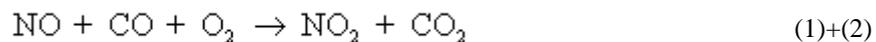
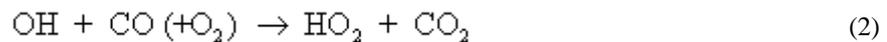
where η gives the ratio of HO₂ at the sampling point to the HO₂ concentrations directly behind the illuminated zone. Without radical losses, η equals 1.

References

Schultz M., Heitlinger M., Mihelcic D. and Volz-Thomas A. (1995) A calibration source for peroxy radicals with built-in actinometry using H₂O and O₂ photolysis at 185 nm, *J. Geophys. Res.*, **100**, 18,811-18,816.

Principle of the chemical amplification technique

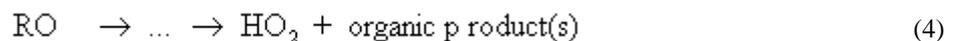
The chemical amplification technique is designed primarily for measuring HO₂. It relies on the HO_x-catalysed oxidation of CO and NO to CO₂ and NO₂ by the following reaction cycle (*Cantrell and Stedman, 1982*):



with: $k_1 = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (*Bohn and Zetzsch, 1997*)

The number of HO_x-catalysed cycles which occurs before radical removal by a termination reaction is defined as the *chain length* (CL), such that the yield of either NO₂ or CO₂ is $CL([\text{HO}_2] + [\text{OH}])$, where [HO₂] and [OH] are the sampled concentrations of these species. CL is therefore an "amplification factor", which allows the quantity ([HO₂] + [OH]) to be determined from measurement of a much larger yield of NO₂ or CO₂, provided the value of CL is known. Under ambient conditions, the concentration of HO₂ is typically much greater than that of OH. Consequently, the amplification technique effectively provides a measure of [HO₂].

However, RO₂ radicals are typically present at a total ambient concentration which is comparable to that of HO₂ (Mihelcic and Volz-Thomas [1994]; Stevens *et al.* [1997]) and are also believed to contribute to the measured signal, because they are readily converted to HO₂ in the presence of NO, via the oxy radical (RO):



The mechanism for conversion of RO to HO₂ depends on the structure of the organic group "R". For simple RO radicals such as CH₃O, the conversion to HO₂ occurs in a single step by reaction with O₂. For more complex RO radicals, the mechanism may be multi-step, involving isomerisation and/or thermal decomposition reactions, and possibly the involvement of further peroxy and oxy radical intermediates, but (in the majority of cases) still ultimately yielding HO₂.

A typical instrument is shown below.

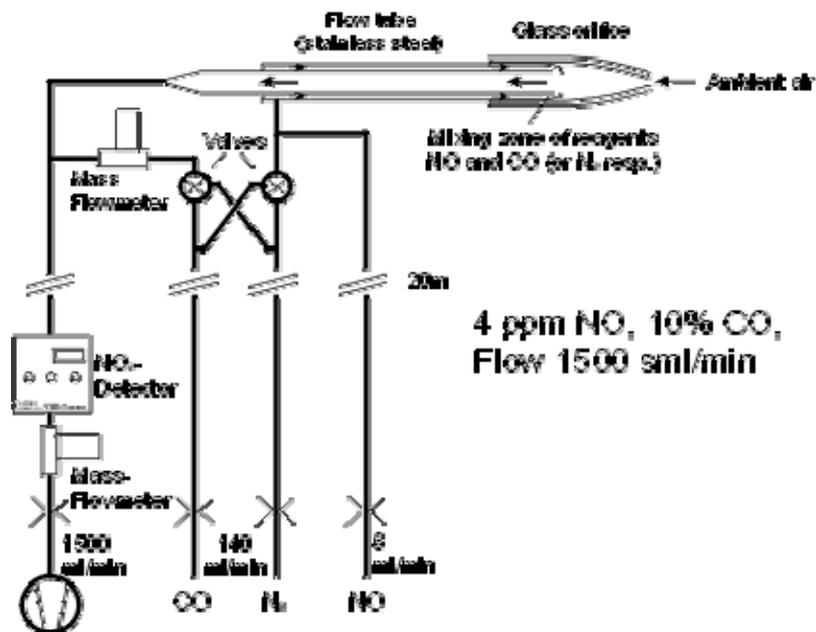


Figure 1: Setup of the chemical amplifier of ICG 2

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Mihelcic D. and Volz-Thomas A. (1994) The ratio of organic peroxy to hydroperoxy radicals: Direct measurements by Matrix Isolation/ESR-spectroscopy, in *Transport and Transformation of Pollutants in the Troposphere, Proceedings of EUROTRAC Symposium '94, Garmisch-Partenkirchen*, edited by P. Borrell, P.M. Borrell and W. Seiler, pp 379-384, SPB Academic Publishing, The Hague.

Stevens P.S., Mather J.H., Brune W.H., Eisele F., Tanner D., Jefferson A., Cantrell C., Shetter R., Fried A., Henry B., Williams E., Baumann K., Goldan P., and Kuster W. (1997) HO_2/OH and RO_2/HO_2 ratios during the Tropospheric OH Photochemistry Experiment: Measurement and theory, *J. Geophys. Res.*, **102**, 6379-6391.

The Sensitivity Of The Radical Amplifier To Ambient Water Vapour

Introduction

As part of the objectives of PRICE II, to better understand the performance of the radical amplifier, laboratory experiments have been performed to examine the sensitivity of the instrument to ambient levels of water vapour. Given the high, and variable, concentrations of water in the atmosphere, any such sensitivity would have a marked impact on the use of the technique in field studies.

Experimental

Experiments were performed on the radical amplifier used by the York University group in the PRICE II intercomparison (Arias and Hastie, 1996). In the basic instrument, NO and CO are mixed with the sample air in a Teflon cross at the inlet to the Teflon tube reactor, to produce mixing ratios of 2 ppmv and 4% respectively. For the water dependency experiments an additional flow of air was introduced at the same point, to allow the addition of water vapour into the reactor. The luminol detector was operated in the linear regime by adding NO_2 from a permeation tube downstream of the reactor.

Mixing ratios 10 to 150 pptv of HO₂ radicals were generated from the photolysis of water in the presence of CO at atmospheric pressure (Schultz et al. 1995) in a copy of the MPI calibrator. This flow was diluted with air saturated with water to give a range of humidities up to around 70%. Experiments using dry air showed the measured concentration of radicals agreed with that calculated from the dilution factor, showing there were no additional radical losses upon dilution. The change in chain length on the addition of water was obtained by measuring the NO₂ produced in the presence and absence of water in the additional air flow. The ratio of the NO₂ produced in the two experiments is the ratio of the chain lengths and, provided the experiments were performed in the linear region of the detector, is independent of the absolute concentration of the radicals and the sensitivity of the NO₂ detector.

Experiments were performed on three different reactors, using the same Teflon cross arrangement described above. No attempt was made to duplicate other inlet designs. The reactors used were: a 3" OD Teflon tubing reactor as used in the field by the York group; a 2" OD Teflon tube which has almost twice the volume to surface area ratio; and a 30 cm long, 3 cm OD glass reactor similar in size and shape to that used in some field studies (e.g. Cantrell et al. 1993).

For measurements of the wall loss rates, an additional length of tubing was inserted between the source and the detector. The variation in radical concentration with length of tubing gave the wall loss rate coefficient.

Results and Discussion

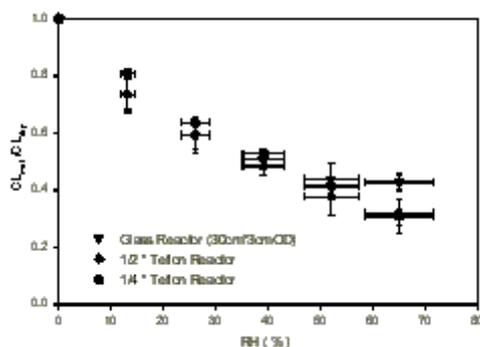


Figure 1: Change in the chain length of the radical amplifier with relative humidity in the reactor. Results for three reactors are shown.

Figure 1 shows the results of the room temperature experiments expressed as the fractional change in the chain length as a function of the relative humidity of the air in the reactor. The data show a significant decrease in the chain length with increasing relative humidity for all reactor geometries. This implies that, if a radical detector is calibrated with dry air (as is usually the case) and the measurements are made at 40% relative humidity, the apparent radical concentration determined by the radical amplifier is only half of the actual radical concentration. Furthermore the chain length is very sensitive to changes in the relative humidity - at around 40% relative humidity it changes by 1% for every 1% change in relative humidity. Since field measurements are made at ambient humidity, and dry gases added to the reactor are at most 10% of the total, this observation suggests that measurements using this technique may underestimate the true radical concentration.

Source of the water dependence

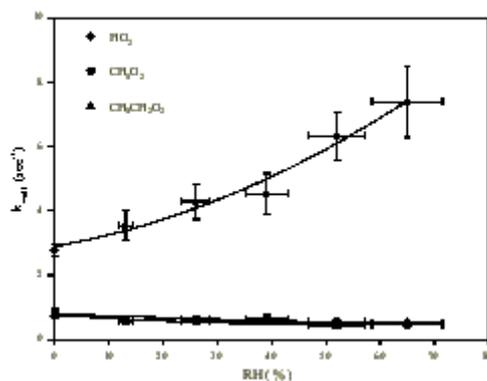


Figure 2: Variation of the rate coefficient for loss of radicals to the wall of the Teflon tube as a function of relative humidity.

The impact of water on the nature of the reactor walls seems the most likely explanation as radical loss to the walls is the dominant loss mechanism in this radical detector. Measurements of the wall loss rate coefficient are shown in Figure 2. For HO_2 radicals, in a 3"OD Teflon tubular reactor, the rate coefficient shows more than a factor of two increase for a relative humidity change from zero to 50%. Note that the organic radicals show no such dependence.

If wall loss is the source of the water dependence its impact could be reduced by heating the walls of the reactor to reduce the amount of adsorbed water. This is supported by experiments which show there is much less impact of water at higher wall temperatures.

If the sensitivity to water is due solely to variations in the wall termination reactions, the impact could be lowered by increasing the importance of the gas phase termination reactions. Additional experiments were performed at an NO mixing ratio of 12 ppmv and they show the chain length has a reduced sensitivity to water. However given the expected dominance of the gas phase radical loss in the presence of higher NO concentrations, this improvement is not as large as would be expected. This has led to suggestions that the gas phase chemistry also has a dependence on water concentration.

Overcoming the water dependence

There are two ways to deal with the water sensitivity. The first is by performing radical calibrations as a function of relative humidity and collecting ambient humidity data in conjunction with the radical measurements. The second is to redesign the radical amplifier to minimise the impact of ambient water vapour. In cases where the termination is dominated by the loss of radicals to the walls, the problem can be minimised by lowering the relative humidity. The reactor could be heated, but this would increase the rate of radical production from stable species such as PAN, and so would compromise the radical measurements in many environments. The reactor could be operated at low pressure, but this would also decrease the rates of all reactions and force a re-evaluation of the technique. The removal of water using membrane tubing or cooling the gas, as in other applications, seems unrealistic given the reactivity of the target radicals. Thus there does not appear to be a universal, simple method to overcome the water sensitivity identified here.

Conclusion

The radical amplifier used by the York group in PRICE II has been shown to be adversely affected by ambient levels of water vapour that could make measurements severely underestimate the actual concentrations. The effect is at least partly due to an increased rate of radical loss to the walls of the reactor in the presence of water, but there also appears to be a contribution by the gas phase chemistry. Additional kinetic data on the reactions of radicals and NO_x in the presence of water are needed. Calibration of this instrument at varying relative humidities appears to be the only method to overcome this problem as no viable method for modifying the instrument is suggested.

Acknowledgement. This work was supported in part by the Atmospheric Environment Service of Environment Canada.

Papers arising from this study

Mihele C. M. and D. R. Hastie, (1998) The Sensitivity Of The Radical Amplifier To Ambient Water Vapour. *Geophys. Res. Lett.* 25,11,1911-1913,1998.

Mihele C. M., M. Mozurkewich, and D. R. Hastie. (1998) Radical Loss in a Chain Reaction of CO and NO in the Presence of Water: Implications for the Radical Amplifier and Atmospheric Chemistry. *Int. J. Chem. Kinet.*, accepted

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The measurement of Cl/ClO by chemical amplification

During Price II the chemical amplification technique was applied in arctic field experiments within the European Community supported ARCTic Tropospheric Ozone Chemistry in spring 1995 and 1996 (ARCTOC, 1997). In February 1996 this ROx-box, and the calibration device were compared to other instruments at the PRICE II intercomparison (Forschungszentrum Jülich). So far a possible sensitivity of the ROx-box towards other species than HO_x and RO_x had been generally ignored.

ARCTOC: during ozone depletion events the signals of the ROx-box increased above normal levels of about 4 ppt RO₂ and also at night the signals were similarly high. Ensuing laboratory investigations showed the ROx-box to be sensitive for OCIO but not for bromine compounds.

A chain reaction involving Cl atoms oxidised carbon monoxide to CO₂ and NO to NO₂ in the presence of oxygen. The kinetics of the combination of Cl-atoms and CO (1) had been described by Nicovich et al., [1990], the addition of oxygen to the ClCO (2) had been found by Ohta, [1983] and the oxidation of NO by the ClCO₃ (3) had been reported by Hewitt et al., [1996].



OCIO is readily reduced by NO to Cl-Atoms (4) and (5). The chain is probably terminated by the formation of nitrosylchloride (6).



Instrument

In the ROx-box as described by Arnold, 1997 a flow of 2000 cm³/min ambient air is drawn through a teflon reaction tube (10 mm wide and 500 mm long). At its end the NO₂ content of the gas is measured by a chemiluminescence detector based on luminol (LMA 3, Scintrex). In order to maintain a chain reaction 160 cm³/min pure CO and 10 cm³/min of a mixture of 400 ppm NO in nitrogen are added at the inlet of the reaction tube. All parts are in a thermostatted box.

Calibration of chainlength

RO_x: The efficiency of the chain reaction or chain length, CHL, is given by the number of NO₂ molecules produced from one primary radical. Calibration for HO_x and RO_x was carried out by the photolysis of a mixture of water vapour and dry synthetic air at 185 nm (Brune et al., 1995; Schultz et al., 1995). An average of 160 ±15 in 1995 and 155 ±10 in 1996 was found for CHL_{perox}. The detection limit was 2 ppt in 1995 and 1 ppt in 1996 (10-minute-average).

Chlorine: A qualitative check of the sensitivity of the RO_x-box for halogen atoms was carried out by diluting 1% Cl₂ in nitrogen by a factor of 1000 in a stainless steel cylinder (6l volume) with dry nitrogen at about 1 bar. This mixture was diluted for a second time in the same way and then the pressure in the stainless steel cylinder was raised from the 1 bar to 3.5 bar by adding dry nitrogen. 3-8 cm³/min of this mixture were passed over heated NaClO₂ at 100° C. Providing a quantitative conversion of the Cl₂ the gas should have contained 5.7 ppb of OClO. Several calibrations were done with that Cl₂ mixture diluting it dynamically with synthetic air to 6 to 20 ppt of OClO. The chainlength, CHL_{Cl}, being than a hundred. Moreover, the RO_x-box indicated no chain oxidation of NO to NO₂ with 1 ppb of Br/BrO_x.

For better accuracy OClO from the reaction of KClO₃ with concentrated sulfuric acid was introduced into a 4 l quartz cell equipped with optical windows for UV absorption measurements. The OClO was determined as 2.13x10³ molec cm⁻³ at room temperature according to its optical absorption band at 378 nm (ϵ = 7.0x10⁻¹⁸ cm², Wahner et al., 1987). Two cm³/min of this mixture were added to a flow of 10 000 cm³/min synthetic air yielding 86 ppt OClO. The calibration of the RO_x-box showed a CHL_{Cl} of 330.

Though at polar sunrise mostly bromine plays a role in the O₃ destruction (Barrie et al., 1988; Martinez et al., 1998; Tuckermann et al., 1997) a certain participation of chlorine had been deduced before from the distribution of hydrocarbons (Jobson et al., 1994; Ramacher et al., 1997).

Apparently the RO_x-box allows sensitive measurements of active chlorine in ambient air and a better insight into the reaction manifold at polar spring was gained (Martinez et al., 1998).

Field measurements

For ARCTOC in spring 1995 at Spitsbergen day profiles of radicals are shown as HO_x/RO_x mixing ratios in Figures 1. During that period several episodes of Cl/ClO were observed in the absence of BrO while the ozone was slightly diminished at the same time. This is taken to be the start of halogen initiation under the influence of ozone and possibly of light.

Discussion

Evidence for active chlorine outside LOEs by RO_x-box: The daily variation of the RO_x-box signal often did not follow J(NO₂) as on most days around the end of May (fig. 1) so that contributions by Cl/ClO are substantial. Clear indication for the presence of active chlorine is found then by the enhanced RO_x-box signals in the nights May 4/7 and 11/15 (figure 1). BrO was zero so that no RO₂ could have been formed through Cl atom abstraction from hydrocarbons. The O₃ had decreased a little (ARCTOC, 1997; not shown here).

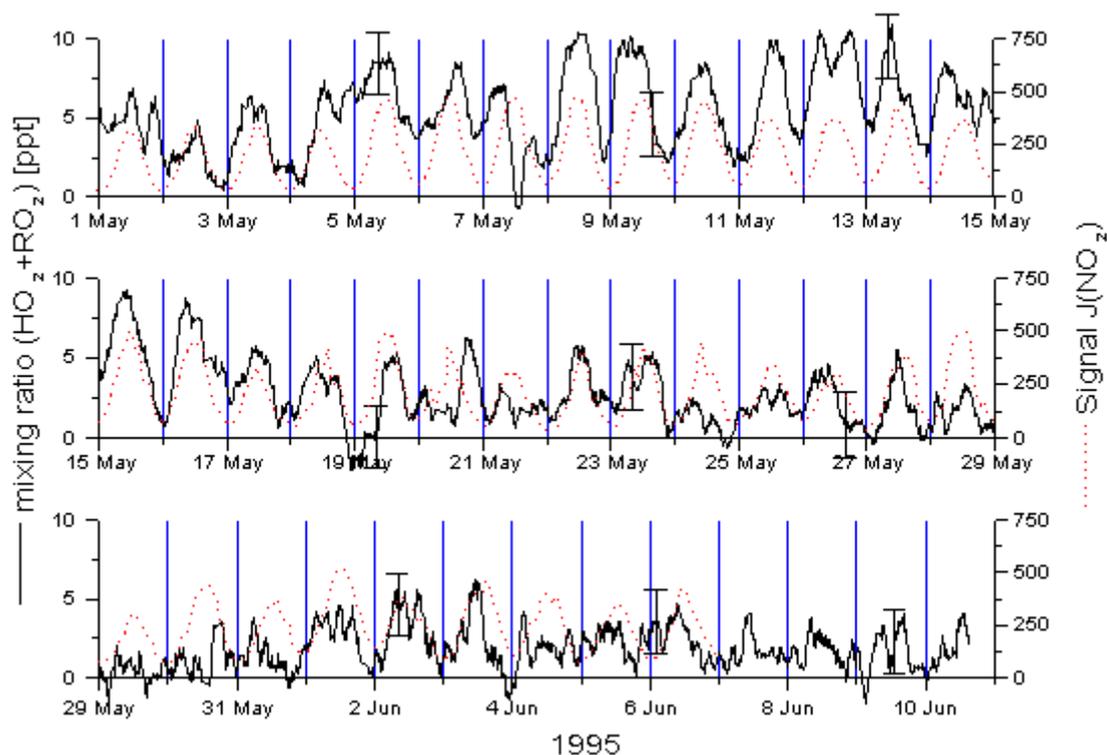


Figure 1: ARCTOC 1995 peroxyradical signals from ROx-box (solid line) calibrated corresponding to HO_x. NO₂ photolysis frequency J(NO₂) (dotted line).

The spectroscopic detection of ClO suffered from low sensitivity (Martinez, 1998) though Tuckermann et al., (1997) were able to extract ClO for LOE periods. Indirect evidence for the participation of chlorine by Ramacher et al. [1997] also supports the observation of chlorine by the ROx-box during those periods.

Role of halogens during ozone depletion: Chlorine is most of the time involved in the ozone depletion. However, its impact in comparison with bromine is small as Cl-atoms are regularly lost through their reactions with hydrocarbons to form HCl. Episodes of Cl/ClO without bromine therefore showed only a small effect upon ozone.

Conclusion

The observation of Cl/ClO by a new ROx-box amplification scheme opens the possibility of in situ measurements of atmospheric active chlorine with a sensitivity of better than 1 ppt at ambient conditions close to the ground. With suitable reaction chambers the chainlength of both amplifications chains for HO_x/RO_x and Cl/ClO could be optimised so that both classes of species may be observed simultaneously in the future. The possible interference of water vapour (Mihele et Hastie, 1998) needs to be investigated.

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Executive Summary

Peroxy radicals (HO_2 and its organic homologues RO_2) are important intermediates in atmospheric photo-oxidant formation. They arise from the oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) by hydroxyl radicals (OH), nitrate radicals (NO_3), halogen atoms and ozone (O_3). Depending on the prevailing NO concentration, ozone and other photo-oxidants, e.g. peroxides, PAN and other organic nitrates, are formed in this mechanism. While atmospheric measurements of OH are essential for establishing the accuracy of the basic theories about atmospheric photochemistry, measurements of RO_2 and HO_2 provide a deeper insight into the mechanism of photooxidant formation, as their concentrations are sensitive to both the chemical composition and actinic fluxes experienced by an air parcel.

Methods to measure the concentrations of free radicals in the troposphere have been sought for almost three decades. For the measurement of HO_2 and RO_2 , only one spectroscopic method exists to date, namely matrix-isolation followed by electron spin resonance spectroscopy (MIESR). It is capable of distinguishing between HO_2 and RO_2 (and NO_3) but its relatively complicated logistics have so far prevented a wide spread deployment of MIESR. An alternative method for the detection of HO_2 is its conversion to OH by reaction with NO at low pressure, followed by detection of the OH by laser-induced resonance fluorescence (LIF). Another indirect technique for detection of HO_2 is the chemical amplifier (CA). It is based upon a chain reaction involving reactions of HO_2 and OH with NO and CO, respectively, and on the measurement of the NO_2 produced. Organic peroxy radicals are also detected by the CA if the primary reaction with NO results in the production of HO_2 . The logistical needs of a CA are much less demanding than those of MIESR and LIF, but because of its complex and non-linear chemistry and the lack of speciation, the CA is subject to a variety of possible sources of error, which include the uncertainty in estimating the amplification factor and the conversion efficiency for organic peroxy radicals.

In order to assess the capabilities and limitations of the different detection and calibration methods for atmospheric measurements, a formal comparison between MIESR and several CAs (PRICE) was conducted in 1994 at Schauinsland as part of the EU-funded project OCTA (EV5V-CT91-0042). Relatively large discrepancies were observed in the atmosphere and for some of the calibration sources used, in particular for that based upon thermolysis of PAN. These differences could not be resolved under the adverse conditions of a field campaign. PRICE II was initiated in order to improve the understanding of the CA and the radical sources used for calibration. The project involved 7 partners from 4 European countries and Canada. The objectives were to

- characterise and compare existing calibration methods for peroxy radicals,
- determine the relative response of the CA for HO_2 and RO_2 ,
- improve the understanding of the chemistry in CAs,
- develop a model of the CA that implements the results from the laboratory study,
- develop a reliable calibration method for field studies, and to
- find optimum operating conditions for the CA with respect to HO_2 and RO_2 detection.

The work programme included a comparison and evaluation of the different calibration procedures used by the partners as well as laboratory and modelling studies of the conversion efficiency for organic RO₂ radicals and of the physico-chemical parameters required for accurate predictions of the HO₂ concentration produced by H₂O/O₂ photolysis. The following results were obtained:

Calibration of the Chemical Amplifier

Three radical sources were evaluated in the project, i.e. PAN thermolysis (PTS), methyl iodide photolysis (MPS) and water photolysis (WPS). The WPS, which is most widely used, is based on the photolysis of H₂O and O₂ at 185 nm. The cross sections of H₂O and O₂, which are essential for the calculation the HO₂ concentration, were re-measured within the project. Although both values were found to be about 30% larger than previously accepted, the ratio of the two values, from which the HO₂ concentration is calculated, did not change significantly. An important finding was that the effective O₂ cross section must be determined individually for each lamp and set up. A computer based model for optimisation of the physical and chemical parameters of the WPS was developed under FACSIMILE by contract to AEA.

Two versions of the WPS were evaluated, one with a laminar flow profile and one with plug flow. On the latter version, the concentrations predicted from theory were in relatively good agreement with those measured by MIESR, i.e. 25% smaller. At the WPS with the laminar flow, the MIESR measurements were almost a factor of 2 larger than those expected from theory. A direct comparison using LIF and CA as detectors gave a factor of 1.5 difference between the two sources, in agreement with the factor determined by MIESR. The reason for the difference is at present unclear, in particular as earlier measurements made in 1994 with similar sources had shown good agreement (<20%) and since LIF and MIESR seem to be in good agreement for atmospheric measurements of HO₂.

The problems encountered in 1994 at Schauinsland with the PAN thermolysis source PTS were successfully solved in the project by reducing the temperature to 120°C. The MIESR measurements agreed with the calculated value within the known experimental errors. Minor problems with the adaptation of the CA to the PTS should be solved by further reducing the temperature. As the PTS is most likely not affected by the presence of H₂O, it is well suited to investigate the influence of H₂O on the CA and offers great potential for calibration in the field, in addition to the WPS. The MPS was found to be more difficult to employ for calibration of the CA because of the complex chemistry involved and because of an artefact signal that is detected with different sensitivity by the different CAs.

Comparison of the NO₂ calibration of the partners revealed significant differences which were caused by the use of NO₂ permeation tubes for NO₂ calibration. In order to improve and ensure the precision of the CA under field conditions, it is strongly suggested that the NO₂ calibration is tied to a primary standard such as a certified NO₂ cylinder or an O₃ calibrator.

Sensitivity of the CA for organic RO₂ and halogen radicals

Modelling studies showed that, in the absence of heterogeneous sampling losses, the CA should measure > 90% of the total peroxy radical population (i.e. [HO₂] + [RO₂]) during the day, and between 70 and 80 % at night. Extensive measurements of the sensitivity for different organic peroxy radicals exhibited much less dependence on the NO concentration than expected from theory. The most likely reason is that the conversion of RO₂ into HO₂ occurs faster than the mixing of the reagent gases, which means the RO₂ are converted to HO₂ at much lower NO concentrations than assumed from instantaneous mixing. The response of the CA to ClO_x radicals was found to be twice as high as that for HO₂. This opens the possibility for investigation of the chlorine chemistry, for example in the polar boundary layer.

Heterogeneous radical losses

Laboratory measurements revealed large differences in the heterogeneous inlet losses for HO₂ and CH₃O₂. Being almost negligible for CH₃O₂, inlet losses for HO₂ were between 15 and 45% for the different instruments. Inlet losses for larger organic RO₂ were found to depend on the structure of the radical and, in particular, on the presence of other functional groups.

A major finding was that the chain length (or amplification factor) of the CA decreases by a factor of 4-6 when increasing the relative humidity from virtually zero to 80%. As a consequence of the calibration being performed in dry air, the actual RO₂ concentration in ambient air (humidity 50-60%) is severely underestimated by a factor of 2-4. The humidity effect is large enough to fully account for the average

differences of a factor of 2 between the CAs and MIESR that were observed 1994 during PRICE in ambient air at Schauinsland. Given the magnitude of the effect and its sensitivity to variations in relative humidity and temperature, correction of ambient data in retrospect seems difficult, as it requires the knowledge of the inlet temperatures of the CAs during the measurements. At present, calibration of the instrument at varying relative humidity appears to be the only method to overcome this problem.

The effect is attributed, at least partly, to an increased radical loss to the walls of the reactor in the presence of water, but there may also be a contribution by gas-phase chemistry. The laboratory experiments indicate a large temperature dependence. Atmospheric measurements also indicate that the influence of humidity can be minimised by operating the CA slightly above ambient temperatures. This solution, however, requires further investigation as the potential influence of thermally unstable compounds, such as PAN and PNA, on the radical measurement needs characterisation.

Dissemination and exploitation of results

The results of the project were extensively discussed on several workshops and two conferences (OCTA, Venice, Oct. 1996 and EGS, Nice, April 1998). Dissemination will continue at conferences and in the scientific literature. Several papers have appeared or are submitted and several more are in preparation. Four Ph.D. theses were completed within the project (*Arnold*, Mainz 1997, *Heitlinger*, Wuppertal 1997, *Arias*, Toronto 1997, *El-Boudali*, Orleans 1997). Exploitation of the results through commercialisation of the instrument requires further research and was not a goal of the project.

Conclusions

Accurate peroxy radical measurements are essential for understanding atmospheric chemistry and in particular for the development of adequate strategies for the abatement of the so-called summer smog problem. The two PRICE studies have resulted in a much improved understanding of the CA technique, the only method currently used which is low cost and readily deployed in a variety of environments. The CA also detects ClO_x radicals which are thought to be important intermediates in polar photochemistry. Problems remain to be resolved but the limitations and advantages of the CA method are, as a result of this study, much better understood.

Recommendations have resulted from the project, which will improve the accuracy and reproducibility of future measurements. These include the use of materials with a high wall recombination coefficient for HO_2 to avoid changes in chain length of the CA during operation. The design should minimise and allow for an independent determination of inlet losses for HO_2 . A reliable and traceable calibration procedure for the NO_2 detector (best via O_3 calibrator) is paramount. The most suitable radical sources for calibration of the CA are PWS and TPS (provided that the minor temperature problem is solved), which is best suited for calibrations at varying humidity.

The significant decrease of the amplification factor with increasing water concentrations means that the method of chemical amplification only yields reliable results when radical calibrations are performed taking the humidity into account. The humidity dependent change in sensitivity needs to be fully understood if the CA is to remain viable. This requires additional kinetic data on the reactions of radicals and NO_x in the presence of water and calls for improvements of both, the CA and of the radical sources used for its calibration.

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