Atmos. Chem. Phys. Discuss., 8, S7276–S7280, 2008
www.atmos-chem-phys-discuss.net/8/S7276/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Airborne measurement of OH reactivity during INTEX-B" *by* J. Mao et al.

Anonymous Referee #1

Received and published: 19 September 2008

General Comments

I enjoyed reading this paper very much. In this paper the first measurements of OH reactivity are made as a function of altitude from an aircraft platform. The OH reactivity represents the rate at which OH is removed from the atmosphere by reaction with its sinks, and provides an additional target for models. Comparison with the calculated OH reactivity using measured OH sinks gives information on whether there are unmeasured sinks. Unmeasured sinks will lead to a model overprediction of the OH concentration when compared to measured OH due to missing sinks in the model. In this paper Mao et al. make measurements of the OH reactivity as a function of altitude, together with OH and HO2 concentrations. Simultaneous measurements of many trace gases and photolysis frequencies enable OH reactivity, OH and HO2 concentrations to be calculated for comparison with measurements, as well as calculation of the rate of production of OH. The measured OH reactivity is compared with two different methods

for calculating the reactivity. The first uses the measured sinks, the second makes use of the steady-state equation for OH : P(OH)=L(OH) = [OH] x OH reactivity, and because the OH concentration has also been measured, is it possible to use the measured production rate (HO2+NO, O1D+H2O etc.) to calculate the reactivity for comparison with experiment. The group has extensive experience with OH reactivity measurements on the ground, but there are considerable complications associated with aircraft operation, for example the change in temperature between the ambient atmosphere and the flowtube in which OH reacts with its sinks, the change in pressure and potential change in the wall loss rate of OH in the flowtube (and associated changes in flow velocity which changes the reaction time) as the altitude changes. An excellent and detailed account of how these difficulties are addressed is given, providing confidence about the accuracy and validity of the results. There is considerable uncertainty in the wall loss, however.

These measurements were taken during the 2nd phase of INTEX with flights largely over the clean Pacific Ocean. The results show that at low altitude, 0-4 km, and particularly in and just above the boundary layer 0-2 km, there are significant discrepancies between the measured and modelled OH reactivity, and OH concentration. The OH reactivity is underestimated in the model, which is consistent with the overprediction of OH. It is thought that unmeasured VOCs are responsible for the missing reactivity, and that these produce HCHO, consistent with the underpredicted HCHO in the model that was also seen. However, this is only one explanation, and further work is needed to identify the unknown chemistry. Near the ocean surface recent work has shown the importance of halogen (bromine and iodine) chemistry in controlling the budget of ozone (see for example Read et al., Nature June 2008), which also has a significant effect on concentrations of HOx. The results of Read et al. suggest this influence extends to the entire tropical marine boundary layer, and possibly there is some influence in the open ocean at higher latitudes also, and so would encompass some of the regions flown in this study. In the current work the model does not contain any halogen chemistry, but mention should be made of any possible influences of halogens on the results

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presented at low altitude, where the discrepancies are largest.

Specific Comments

Abstract should contain information on which geographical region the measurements were made in.

Outliers in the decay could also be caused by fast changing drifts in laser power or wavelength, were these ruled out (photodiode or reference cell measurments to check this)

The flow is close to laminar, and theory is used to suggest the type of radial flow velocity profile in the flowtube. Is there experimental evidence to support this? e.g. from radial profiles for long-lived gases injected from the injector and mixing with the main flow?

The section on possible interference from the HO2+NO reaction needs further detail. —does not make much OH in the flow tube—. What does —much— mean? It is crucial to understand any recycling from this reaction, and so some numbers need to be given as to the effect of this reaction, even if it is very small. What is the (small) error by not correcting for it?

It is very difficult to get very clean carrier gases (or to scrub them sufficiently at the large flow rates needed) and so impurities and hence OH reactivity from impurities is inevitable. The alternative way to get the wall loss rate, by subtracting the calculated reactivity from the measured value in clean ambient air, does have problems if there are unknown OH sinks in the —clean air—. As shown in this work, even in the clean Pacific, there are considerable unmeasured OH sinks (at least at low altitude), and so using this air for calibration of the wall loss with altitude is not ideal.

There is another method to calculate the OH reactivity which is mentioned briefly later, which is to use a detailed model to calculate not only the OH reactivity from measured sinks, but also the OH reactivity from additional sinks generated from the oxidation of these primary sinks (i.e. intermediates and end products). However, the rate coeffi-

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cient for OH + these species is often not known. It would appear the inclusion of the intermediates and end products does not make a significant difference to the OH loss rate in this study, but this is only covered briefly and should perhaps be expanded upon.

Why does the concentration of reactants decrease by 10-15% in the flowtube? Is this because of removal by OH or other physical mechanisms, or due to dilution as gas is added via the injector?

If the air warms by 50 degrees, does this have any impact on some sinks that could decompose between the inlet entrance and when OH is added to the airflow? If the decomposition products react differently to the initial molecule this could have an effect. This would depend on the transit time.

Near the ocean surface the presence of BrO and IO could have an effect on HO2 (especially) and OH radical concentrations. Reaction of HO2 with these species recycles OH (after photolysis of the formed HOI or HOBr). (Read et al Nature, June 2008). Is an influence of halogen chemistry likely to alter the model-measurement comparisons for OH or HO2 or the major conclusions of the paper for the lowest altitude?

OVOCs have been shown to be more dominant than NMHCs for OH removal in clean, marine environments from other studies and some further references should be included.

Figure 8 . Some comment on the variability of OH, HO2 and HCHO for these plots is needed. For a given altitude, were the measurements made at a similar time of day, or quite different?

Technical Comments

There are typos in the paper, —the— is missing in line 3 of the abstract for example, and in the first line after equation (1), so a careful check is required.

Table 1. H2O2 and CH3OOH (rather than CH3COOH)

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As colour is used, suggest in the captions for figure 2 and 7 that the colours are stated together with the type of line and symbol for clarity.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14217, 2008.

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