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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Design of and initial results from a highly instrumented reactor for atmospheric chemistry (HIRAC)” *by* D. R. Glowacki et al.

D. R. Glowacki et al.

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Referee Comment: As discussed by the authors, one of the greatest strengths of HIRAC is the ability to measure OH directly, which constrains the chemistry substantially and allows for absolute rate measurements of OH reactions. But the studies presented as a demonstration of pressure-dependent kinetics in HIRAC are relative rate studies, using Cl atoms as the oxidant. The paper would be much stronger if it had at least one absolute kinetics measurement, combining the best features of the chamber into a single study.

Response:The objective of the paper is not to present any detailed results on any particular studies, but rather to demonstrate the capabilities of HIRAC, including OH

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detection, from some relatively straight forward systems. HIRAC is able to undertake both kinetic and mechanistic studies; we envisage that the relative rate method will be an important method of generating kinetic data and have therefore presented kinetic results using this technique. Absolute measurements have been obtained for the reaction of O3 + t-butene, and are planned for a new NO3 detection system.

As the reviewer correctly points out, absolute time resolved OH and HO2 measurements are extremely helpful in constraining a chemical model and an example of this has been presented. The OH detection system is currently being refined, and this paper paves the way for subsequent studies of absolute rate measurements of OH reactions.

Referee comment: However, no NO2 actinometry results are presented for comparison; these would be very useful as a first check of the validity of the model.

Response to referee: (text will be amended in final version) Since receiving this comment, the NO2 photolysis rate in HIRAC has been measured to be ˜2.2 x 10-3 s-1, which is about a factor of 3 smaller than JNO2 calculated using the measurements of photolysis frequency on a single lamp. The likely cause of this discrepancy is due to the UV lamps being used at non optimal temperatures. The output from this type of lamp is very dependant on temperature. The conditions in which the single lamp was measured were essentially ideal; whereas the lamps situated in HIRAC are operating under higher temperatures. Thus, we would like to rework the section on the photolysis model, presenting the measurements of the JNO2 measurements, and normalizing the relative values generated from the ray trace simulations to the experimentally measured value.

The Referee suggests including a lamp spectrum.

Response to referee (text will be amended) Since receiving this review, we have taken a spectrum of the lamps, which we will add to the paper. Additionally, we will change the text on p 10695 to refer to ’blacklamps’.

Referee comment: It is mentioned that temperature may be varied, but approximate temperature ranges are not given.

Response to the referee: The chamber has been designed with the potential for temperature variation, however, insufficient funds were available in the construction grant to purchase an appropriate chiller/heater. We envisage that the chamber should be able to operate from 220 -350 K. We will amend the text to emphasise that temperature control has yet to be implemented.

Referee comment: As is standard for LIF instruments, HO2 is measured by titration of the sample with NO to form additional OH. In the case of a reaction chamber with ppm levels of hydrocarbons, RO2 radicals would probably also be detected. A brief discussion of the sensitivity of the instrument to RO2 radicals would be useful. (Was the FAGE instrument running during the Cl kinetics experiments?)

Response to referee (text will be amended): We and other groups have investigated the effect of RO2 radicals on the atmospheric detection of HO2. The NO conversion of HO2 is performed in a low pressure fluorescence chamber; the pressure is about 1 Torr. Thus, although RO2 will be converted into RO quite readily, the reduced pressure means that the rate of RO + O2 to give HO2 is quite slow. The rate of this would still be quite slow even if RO2 (and hence RO) is high. During an intercomparison between the Leeds FAGE HO2 instrument and the PERCA RO2 instrument, here in Leeds, we used the PERCA RO2 source (CH3O2, generated from CH3I photolysis to give CH3+I, then CH3+O2 to give CH3O2) to provide a source of radicals. FAGE did not detect a signal due to CH3O2 (exact [RO2] not known but likely to be in the range 0 - 100 ppt). The level of interference depends on the relative ratio of RO2 and HO2. Clearly, in experiments involving higher concentrations of RO2, interference could be an issue, but the levels of HO2 are also likely to be higher, and the effect of RO2 interference on any HO2 measurements is expected to be minor. In any detailed study the relevant chemistry of HO2 conversion and RO2 interference would be modelled under the precise conditions of the HIRAC measurements. RO2 radicals will not interfere under the current conditions. We are also developing an instrument precisely to measure partially speciated RO2 radicals, which has a pre-reactor at higher pressure (50 Torr) to effect the conversion of RO2 into HO2, before sampling into FAGE where HO2 and OH can be measured. If successful, this instrument would also be used in the HIRAC chamber, and it would be possible to measure the relative amounts of RO2 and HO2. The FAGE instrument was not running during the Cl kinetics experiment.

Referee comment: Do the components internal to the chamber introduce substantial surface area?

Response (this material into the text on p 10694): The volume of the chamber is ˜2.25 m3. The internal surface area of the chamber itself is approximately 10 m2, with the lamp tubes (quartz) adding an additional 2.5 m2 surface area and the fans and mirrors giving an additional 0.5 m2. The total surface to volume ratio is therefore 13 m2/2.25 m3 = 5.8 m-1.

The referee asks for more descriptions of the lamp arrangements.

Response: The total length of quartz tube within the chamber is 200 cm. The total length of the fluorescently coated sections of lamps is 169.5cm, giving an 85% coverage. The lamps are even distributed so there should be no significant axial gradients. We will submit an improved version of figure 1 which should show more clearly the layout of the lamps.

The referee questions what is meant by the phrase ’Cl2 was very stable’

Response: We will rephrase to: (2) Experiments carried out by introducing the reagents into HIRAC the previous night, and then carrying out the irradiations the following morning, gave results in good agreement with those where the irradiations were performed immediately following reagent mixing. We are not able to directly measure how much Cl2 was lost to the walls overnight, but the results suggest that any uptake has a negligible effect on the kinetic measurements.

The referee suggests that the quality of the figures could be improved. Colour figures will be used in the final submission.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10687, 2007.

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