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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.

Anonymous Referee #2

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In this paper, the design and testing of a new reaction chamber for gas-phase kinetics and mechanistic studies are described in detail. Among the key features of the chamber are spectroscopic measurements of OH and HO_2, which will provide substantial insight into the observed chemistry, and control of pressure and temperature, allowing for reactions to be run under a range of atmospheric conditions. The design and characterization of the various elements of the reactor were carried out with great care, and the initial results presented demonstrate the promise of the instrument. It is an excellent instrument paper, and the manuscript is certainly worthy for publication in Atmospheric Chemistry and Physics. I believe the paper could be improved (and would be of greater interest to the general readership of ACP), by (1) presenting additional

experimental data, and (2) placing a bit more focus more on the details of the reactor which are of central interest to atmospheric chemists.

(1) Additional results.

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.

Additionally, a very detailed model of the radiation field within the chamber is put forth. This allows for calculation of J_{NO2} as a function of position within the chamber, and hence for the average J_{NO2} throughout the entire chamber volume. However, no NO_2 actinometry results are presented for comparison; these would be very useful as a first check of the validity of the model.

(2) Additional experimental details.

- The model number and rough spectral range of the photolysis lamps are given (p. 10695). It would be worthwhile to refer to them as “blacklamps” here, and possibly also provide an output spectrum, to give the reader some idea of the type of photochemistry which can occur inside.

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

- As is standard for LIF instruments, HO_2 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, RO_2 radicals would probably also be detected (for example, in the ozonolysis reaction system described near the end). A brief discussion of the sensitivity of the instrument to RO_2 radicals would be useful. (Was the FAGE instrument running during

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the Cl kinetics experiments?)

- Do the components internal to the chamber (lamp tubes, fans, mirrors, KF ports, etc) introduce substantial surface area?

Other comments:

P. 10693, lines 16-26: these detailed descriptions of other chambers are probably not necessary.

P. 10695, lines 24-27. It is difficult to visualize the lamp arrangement based solely on this description. (An improved Figure 1 would aid in this.) Also, are there substantial gaps between lamps within a single quartz tube? If so, this might this lead to axial gradients in the radiation field, which are not discussed.

P. 10697, lines 7-10: the point of this example is not clear. From this single example, one might infer that chambers generally have J_{NO2} values which are too low, but this is not always the case [Cocker et al 2001].

P. 10715, line 1: What does "Cl_2 was very stable" mean? I assume this is in reference to chemical losses, leaks, etc; it should be specified that the lights are off. Moreover, given the reaction conditions, a loss of 50% of the Cl_2 overnight would probably not lead to an appreciable change in the results.

P. 10718, line 14: given that details of the chemistry are not the focus here, it may be clearer to simply state that MCM predicts the OH yield to be 57%. Also, the first OH concentration (line 16) should be specified as the modeled value.

Fig 1: The diagrams are of rather low contrast and resolution, limiting their usefulness (particularly with regards to the position of the lamps and mirrors). Color and/or labels would be very useful.

Fig 10 caption: the reaction studied should be mentioned.

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