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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: It was not immediately obvious that the three lamps in each quartz tube are oriented end-to-end.

Response: Rephrase to : Light for photochemical studies is provided by 24 TLK40W/05 actinic UV lamps, each of length 565 mm (spectral output 300 - 420 nm) housed in 8 quartz tubes (3 lamps orientated end to end in each tube) that are...

An improved version of figure 1 should also help clarify the layout.

Referee comment: P10709, bottom; Isn't the N2O actinometry more complex that what is shown here.

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Response to referee: Agreed, this is a mistake in the paper. We have taken out QY(NO),184.9 nm = 2, and instead made reference to the Edwards paper, which treats the relevant details of the calibration mentioned by the referee.

Referee comment: The linearity checks are certainly worthwhile but would be more informative if absolute IR cross sections or similar could be compared with literature data.

Response: We are currently in the process of comparing our spectra with literature cross sections of O3 and CO included in the HITRAN database, and will comment on the agreement between our measurements and literature values in the revised version. The important point that we wanted to emphasise was the linearity of the measurements, wherever possible we will try to undertake direct calibrations to avoid any uncertainties in resolution, cross section or pathlength.

p. 10714 - Could FTIR have been used here to provide a comparison with the GC data?

Response: Yes, this could have been done, but at the time of those experiments the FTIR was temporarily unavailable. In the next section on the Cl + ethene reaction we do report results from both techniques which are in good agreement.

Referee comment p.10715; Can the chamber operate at higher pressures?

Response: Potentially this is possible; we might have to look at the design of some of the windows and flanges. However, at the moment we don't have a Lloyd's certificate for the welding, so we can only work below atmospheric pressure. It would be really very expensive to upgrade for high pressure work and we have plenty to do at 1 atm and below!

The referee comments on the uncertainty in the reference reaction Cl + chloroethane.

Response: We are aware that there is a degree of uncertainty in this rate coefficient. We have clearly stated the value used to put the tabulated relative rate data onto an

ACPD

7, S5051–S5053, 2007

absolute scale, so the interested reader could modify the results in the light of any future definitive study of Cl + chloroethane. Unfortunately there are relatively few reference compounds that have comparable rate coefficients to the low pressure ethene values that were available and that could easily be used in our column. The uncertainty in the chloroethane rate coefficient was one of the reasons that we used two different references. If we compare the absolute rate coefficients averaged at each pressure from using chloroethane as a reference (with a rate coefficient of either 1.15 x 10-11 or 8.0 x 10-12) or with isobutene as the reference, then we see that the isobutane results lie in between the two chloroethane, but do appear to be more consistent with the higher value. (We have assumed that there are no systematic errors in the method of determination (FTIR or GC) or the Cl precursor and hence different experiments can be averaged for a given pressure and reference reaction.) . This paper is probably not the right place to this issue, but we will add an additional paragraph at the end of the discussion (old p10716) to the final manuscript.

Additional paragraph to be added in final manuscript We are aware that there is some controversy as to the absolute value for the rate coefficient for the Cl + chloroethane reference reaction. Unfortunately only a limited number of reference compounds are available for the Cl + ethene reaction at low pressure. We have used a value determined in a relative rate study against ethane (Wallington et al., 1990a). Direct measurements (Bryukov, M.G. ; Slagle, I.R.: Knyazev, V.D. JPCA 107 6565-6573 2003) report a value of approximately 8 x 10-12 cm3 molecule-1 s-1, some 30% lower. Our absolute values for Cl + ethene from both reference compounds are consistent if the higher value for Cl + chloroethane is used, although the errors are of the order of ś 20%, i.e. comparable to the systematic errors in the Cl + chloroethane rate coefficient. This issue will be addressed in further studies on Cl atom kinetics.

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

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7, S5051–S5053, 2007