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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Near-UV photolysis cross sections of CH_3OOH and $HOCH_2OOH$ determined via action spectroscopy" *by* C. M. Roehl et al.

Anonymous Referee #1

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The authors have embarked on measuring photolysis dissociation cross sections (as a function of wavelength) of a substance using a technique in which the yield of the photo product is measured relative to that observed in a reference compound which also yields the same photo product. The analysis requires that both the quantum yield of the photo product and the absolute absorption cross section for the reference compound be known accurately as a function of wavelength. If there is only one photolysis channel in the wavelength region being investigated, then the measured photolysis dissociation cross sections represent absorption cross section values for the substance under consideration.

In principle, the method described here allows the accurate measurement of low absorption cross sections. Such values are useful in the accurate tropospheric photolysis

rate calculations and in laboratory calibration studies.

The length, the layout and the material discussed are appropriate for ACP publication.

However, the authors need to clarify/state/re-examine the following before the paper can be published.

(1) The authors should point out that both the reference and the test compound are being dissociated under optically thin conditions for equation 4 to be valid.

(2) While the absolute OH quantum yield can be assumed be 1, 1, and 2 for MHP, HMHP and H2O2, respectively, the photolysis in each case can yield different vibrational state distributions in OH. Therefore it is crucial that any vibrationally hot OH be accounted for in the (0-1) detection scheme being employed. In other words, hot OH needs to be quenched. The authors mention that the OH will be relaxed. This is not the case for the time delay of 1 micro-sec that they use. Nitrogen is not a good quencher for OH(X, v"). At 30 torr of N2, and kq,v" =1 of 1 x 10-14 cm3 molecule-1 s-1 to relax OH(v"=1), the lifetime for OH(v"=1) is 103 micro-sec. If we assume that the peroxides are efficient quenchers (1 x 10-11 cm3 molecule-1 s-1) then the lifetime for OH(v"=1) is reduced to 50 micro-sec for the highest concentrations of peroxides used. To overcome this difficulty one should use excess water (a good quencher of OH(X, v") in the back-to-back experiments, and record the time profile of [OH] and extrapolate it to time zero to measure the initial OH yields. This approach will avoid any systematic errors in OH yield measurements due to small OH(v">0) production in the photolyses.

(3) The authors need to explain why they see a large diffusional loss rate in 30 torr of N2, or is there a significant contribution from reaction with back-ground impurities for the minute peroxide concentrations being employed.

(4) The authors should clarify the text, "Advances in laser technology....." Alternatively, they should determine the OH detection sensitivity of their apparatus for the conditions being employed and then use equation 3 to get a better idea of the limit

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in cross section measurements possible by knowing c(lambda) which takes into account the max photon fluxes available for their laser systems before interference from 2-photon dissociation and or LIF saturation sets in.

(5) The one standard deviations reported in figure 2a should be quantified in terms of absolute percentage errors and reported in the corresponding table 1, as well as in figure 2b and table 3. Are the data sets being compared within reported experimental error limits? Error bars should be shown in figures 4a and 4b, and the significance of the reported increase in the total J values for MHP and HMHP discussed in terms of the reported errors and the total loss rate in the troposphere.

(6) What is the likely explanation of the increase in the H2O2/MHP cross section ratio at lower temperatures?

Minor points

P11604 line 1; should read: .....walls, it was necessary.....

P11604 line 4; should read: .....chamber led to an.....

P11607 line 4; should read: .....and recently by Matthews et.....

P11607 line 9; should read: .....greater than the.....

P1163 table 1; should read: .....Vaghjiani.....

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11597, 2006.