Atmos. Chem. Phys. Discuss., 6, S6704–S6706, 2007
www.atmos-chem-phys-discuss.net/6/S6704/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Daytime tropospheric loss of hexanal and *trans*-2-hexenal: OH kinetics and UV photolysis" *by* E. Jiménez et al.

E. Jiménez et al.

Received and published: 8 February 2007

General Comments:
The authors really appreciate the referee's comments on our manuscript. All suggestions and comments will be taken into account (and included) in the preparation of the final version of the manuscript. Also, all small changes and issues listed by the referee will be included.

Specific Comments:
1) **OH Concentration and its Possible Secondary Chemistry**
Hydroxyl radical concentration, generated by photolysis of H2O2, ranged from 3x10(11) to 1.1x10(12) cm-3. Typically, OH concentrations were between 3x10(11) and 7x10(11) cm-3 to ensure that there is no interference of secondary chemistry. However, some experiments were performed at concentrations up to 10(12) cm-3 to

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check for this possibility. Under these experimental conditions no significant influence of secondary chemistry was observed. A null intercept of the k'-k0 versus [aldehyde] plots (see Figure 3) indicates the little (or absence) of a secondary chemistry. As suggested by the referee, a discussion of potential interferences from OH secondary chemistry will be included in the final version of the manuscript. Also, an example of the pseudo-first order decays will be included in it.

2) **Loss of Aldehydes during the Kinetic Experiments**
During the kinetic experiments, no significant loss of aldehyde was observed in the reaction cell. The differences observed before and after entering the reaction cell were independent of laser fluences employed (1.3-20 mJ pulse-1 cm-2). Based on the laser fluence range and the measured absorption cross sections at 248 nm for both aldehydes, we would expect a loss lower than 1 per cent.

3) **Reaction Mechanism**
The negative temperature dependence observed in the OH-reactions of hexanal and trans-2-hexenal is similar to other aldehydes (see below). In all cases, activation energies are negatives and similar for the saturated and unsaturated aldehyde.

Saturated Aldehyde (Ea/R (K)): propanal (-405), pentanal (-305), or hexanal (-565) *Unsaturated Aldehyde* (Ea/R (K)): acrolein (-333), crotonaldehyde (-533), trans-2-pentenal (-510), or trans-2-hexenal (-455).

At room temperature, our results are consistent with the values obtained from the structure-activity relationship (SAR). For hexanal, SAR method predicts that 77 per cent of the H-atom abstraction occurs in the aldehydic group. The rate coefficient for the OH-reaction is 2.19x10-11 cm3 molecule-1 s-1 (27 per cent lower than our experimental data). For trans 2 hexenal, SAR predicts that the rate coefficient for the addition to the double bond is 2.17x10-11 cm3 molecule-1 s-1 and 1.93x10-11 for the

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H-abstraction channel. That means that the addition channel is expected to be more than 50 per cent of the total rate coefficient (4.1x10-11 cm3 molecule-1 s-1). This rate coefficient (although, 14 per cent lower) is in excellent agreement with our experimental results.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 13225, 2006.