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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Kinetic study of the gas-phase reaction of atomic chlorine with a series of aldehydes" *by* D. Rodríguez et al.

D. Rodríguez et al.

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(Anonymous Referee 1)

- The corresponding ranges of concentrations for the aldehydes, reference compounds, Cl-atom source, etc. are given in Table 1. However, a new phrase has been introduced in the experimental section of the revised manuscript to indicate it properly.

- Thèvenet et al. carried out a study of the reactions of Cl with different aldehydes at room temperature and using a relative method. These authors used different reference compounds, ethane, propane and n-butane. Concerning the unsaturated aldehydes, acrolein and crotonaldehyde, the measured rate constants, 2.2 x 10-10 and 2.6 x 10-10 cm3 molecule-1 s-1 respectively, are comparable to the rate constant of the addition

channel of the Cl + propene reaction, 2 x 10-10 cm3 molecule-1 s-1, which dominates at atmospheric pressure (please see International Journal of Chemical Kinetics 32, 676, 2000). The authors explain the difference between acrolein and crotonaldehyde compared to that of propene by the contribution of the H-atom transfer form the -C(O)H group in both aldehydes and in addition from the -CH3 group for crotonaldehyde In this sense, also in that study the rate constant increase when the length of the organic chain increases, kacrolein $<$ kcrotonaldehyde. The same trend is observed in our work as explained in the text. Despite, the values obtained by Thèvenet et al. for Cl + acrolein and crotonaldehyde are higher than the larger unsaturated aldehydes studied in our work and we have not found any obvious and definitive explanation for this fact. In any case, the rate constant obtained by Thèvenet et al. in the Cl + n-pentanal reaction for example, 2.6 x10-10 cm3 molecule-1 s-1 is in excellent agreement with our value 2.56 x 10-10 cm3 molecule-1 s-1. Also, as commented by Referee 3, our obtained constants for n-hexanal and n-heptanal (in cm3 molecule-1 s-1) (2.88 ś 0.37) x 10-10 and (3.00 ś 0.34) x 10-10 respectively, agree within the combined error limits with the constants reported by Plagens (PhD thesis, 2001), (3.23 ś 0.15) x 10-10 and (3.53 ś 0.10) x 10-10 (in cm3 molecule-1 s-1), respectively.

Technical comments:

- Page 5169, line 9: n-pentanal is used for consistence with the rest of paper.

- Page 5170, line 6: “no reactant is reformed” now appears instead of “no product is reformed”

- Page 5170, line 12: “experiment“ is replaced by “experiments”.

- Page 5170, line 24: “under the experimental conditions” is included.

- Bottom of page 5173: the phrase “but was not observed” has been added to the end of the sentence on line 28.

- Page 5174, line 1: “of the decreaseĚ” is replaced by “for the decreaseĚ”.

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- Page 5174, line 20: the rearrangement suggested by the referee has been now made.

- Page 5175, line 2: “chlorine may originate from” now appears instead of “chlorine may be originated from“.

- In Table 2, the last column has been now corrected. The correct ratios are kadehyde/kalkane (or kadehyde/kalkene) instead of kalkane/kaldehyde (or kalkene/kaldehyde). Please see Table 2 in the revised manuscript.

(Referee 3)

- The rate constants of the reactions of Cl + aldehydes were measured using three reference compounds, ethane, propene and 1-butene, in order to check if the results were consistent. As mentioned by the Referee, consistent results have been obtained for each aldehyde with all the reference compounds The plot of ln([aldehyde]0/[aldehyde]t) vs. ln([reference]0/[reference]t) yields a straight line with the slope of kald/kref, showing in all cases a good linearity which suggests the absence of possible problems. The slopes of such sets were calculated using a weighted linear least-squares fit and the quoted errors in the final results are 2. Also, the obtained results were independent to the bath gas used, air or N2 and so the reported kinetic rate constants are the average values in Table 1.

- The values mentioned by the Referee of the rate constants for n-hexanal and n-heptanal reported in the PhD thesis by Plagens (2001), and unknown by the authors because this thesis is in german and the results, as far as we know, are not published in any international journal, have been incorporated in the revised manuscript. Also the new reference (Plagens 2001) has been incorporated in the section “References”. Please see text in the revised paper.

- Page 5170 (line 25): Relative rate experiments were carried out in air or N2 to check the potential interference from OH chemistry as mentioned in the manuscript. In spite of the problem mentioned by the Referee, that chambers with a NOx history are also

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capable of producing OH radicals, any problem has not been detected on the matter. On the other hand, as it is pointed out in the paper, and in the above comments to Referee 1, the rate constants measured in the present work for n-pentanal are in excellent agreement wit the same value obtained by Thèvenet et al. Also, as commented by Referee 3, our obtained constants for n-hexanal and n-heptanal agree within the combined error limits with the constants reported by Plagens (PhD thesis, 2001).

- On the subject of checks for possible interferencesĚ: Concerning the photo-induced isomerisation to the corresponding cis isomer, in the “text experiments” to quantify losses of the trans isomer due to photolysis in the absence of Cl atoms, we did not observe a decay in the signal of the reactant nor the formation of new peaks which could correspond to the cis isomer. The reason for the discrepancy with the results found by Plagens may be due to the differences in the irradiation conditions. In our experimental conditions, the mixture in the smog chamber is exposed to irradiation from fluorescent lamps (Philips TL/05, 20W) with a maximum at lmax=370 nm to phptolyse Cl2. In the experiments conducted by Plagens, solar irradiation is used. Under such conditions the intensity of radiation in the range 300-330nm (where the aldehydes absorption cross sections are significant) is much higher and may so induce measurable rates of isomerisation. Following the suggestion of the Referee, we have introduced a new paragraph recognizing the role of photolysis: In the introduction. Line 21: Ě (Prates et al 1998). In relation to the tropospheric sinks, carbonyl compounds generally show a weak absorption spectrum in the region 220-370 nm resulting from a dipole forbidden n - * transition which may lead to photo-dissociation, generating organic free radicals in the lower troposphere. In the discussion: Ě(Noxon, 1983) and [O3] = 7.4 x 1011 (Logan, 1985) (in units of molecule cm3). Furthermore, Martínez et al and Plagens have reported the absorption spectra of several aliphatic and unsaturated aldehydes and ketones. These compounds absorb actinic radiation in the range 270-340 nm and so the estimates about the degradation under atmospheric conditions must include the photolysis contribution. In this sense, Plagens reports photolytic lifetimes of 15 and 10 hour for hexanal and trans-2-hexenal, respectively. These data suggest

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that photo-dissociation and gas-phase reactions with OH radicals will dominate over reactions with Cl atoms and NO3.

- Page 5174 (line 20-25): We do not quite understand what the referee means. First, the referred page should be 5173. Second: the reactivity trends of the aldehydes towards to be evaluated should be towards Cl and not towards OH?. We think that our contribution to the database of unsaturated aldehydes is not wide enough to enable reliable reactivity factors and quantitative predictions. In this sense we have not included SAR calculations.

- Additional text has been added in the Atmospheric implications (Section “Results and Discussion”) to cover the point commented by the reviewer about the importance of photolysis of aldehydes. The results obtained by Plagens (2001) and commented by the Referee are now included (Please see revised manuscript).

- Page 5175 (line 10): As requested by the Referee in its comment, additional text has been added in the Result a Discussion section (last paragraph) about this subject (please see revised manuscript). Also the new references suggested by the Referee are now included.

- The “Radical” column in Table 2 has been deleted.

- (Final Comment): We also apologize for the typographical and grammatical errors found that we have tried to correct in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5167, 2005.