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

Anonymous Referee #3

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The paper reports on rate coefficients determined for the reaction of Cl atoms with a number of saturated and unsaturated long chain (C5 to C7) aldehydes. The rate coefficients were determined by the relative kinetic technique in a Teflon chamber at room temperature using GC-FID for the analysis. Three reference compounds have been used in the analysis and, with the exception of trans-2-heptenal, relatively consistent results have been obtained for each aldehyde with all the reference compounds. For trans-2-heptenal there appears to be a larger difference between the determinations with the individual references than for the other aldehydes. However, since no errors are included for the rate ratio (kald/kref) values it is not possible to judge the quality of the rate determinations with the individual reference compounds. The errors for the

rate ratio (kald/kref) values should be included in Table 1.

The authors write that they believe that, apart from Cl + pentanal, theirs are first-time determination of the rate constants. I have made a search of the web and a found a PhD thesis by H. Plagens (2001) in which rate constants are reported for some alkyl aldehydes. The thesis can be downloaded from: http://elpub.bib.uni-wuppertal.de/edocs/dokumente/fb09/diss2001/plagens;internal&action=buildframes.action. The thesis is unfortunately in German, however, an English abstract is available. Plagens report the following rates (in cm3 molecule-1 s-1): butanal (2.21  0.16) Œ 10-10, hexanal (3.23  0.15) Œ 10-10, heptanal (3.53  0.10) Œ 10-10, octanal (4.34  0.20) Œ 10-10, nonanal (4.82  0.20) Œ 10-10. Plagens determined the rate constants in a chamber using the relative rate technique and FTIR for the analysis analysis. They employed 1,3-buradiene as the reference compound. The values obtained by Plagens for hexanal and heptanal are around 12 and 18% higher than those reported for the same compounds in the present paper but agree within the combined error limits of both determinations.

Page 5170 (line 25): the authors write that the experiments were performed in air and N2 to check for potential interference from OH radicals. I would like to point out to the authors that chambers with a NOx history are also capable of producing OH radicals in N2 due to NOx memory effects and HONO production at the chamber wall. This capability can persist for a very lengthy period after cessation of NOx use.

On the subject of checks for possible interferences in the kinetic experiments did the authors check for possible cis-trans isomerisation upon irradiation with their lamps of the trans unsaturated aldehydes investigated in their study. Plagens (2001) observed cis-trans isomerisation of trans-2-hexenal in the EUPHORE chamber in Valencia Spain.

Page 5174 (line 20-25): It is obvious that for the unsaturated aldehydes that abstraction from the -CHO and addition to the -C=C- entities dominate the reaction mechanism and that the rate coefficients for each mechanistic element are fairly similar. The values

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reported here are very similar to those reportd for Cl + acrolein, crotonaldehyde and pivalaldehyde by Ullerstam et al. (PCCP 3 (2001) 986). Plagens (2001) has used the "Structure Activity Relationship (SAR)" to calculate the relative contributions of H-atom abstraction from the CH3-, -CH2- and -CHO entities in a series of alkyl halides. I am quite sure that there is sufficient information available to make sound "guessimates" of the contributions of H-atom abstraction by OH and OH addition in the reactions of OH with the unsaturated aldehydes investigated by the authors, which would demonstrate quite clearly the reactivity trend (or lack of it) for these aldehydes.

The paper completely ignores the importance of photolysis of aldehydes as a sink for aldehydes both in the Introduction and in the discussion of the atmospheric lifetimes of the aldehydes. Plagens(2001) for example and measured 4 h and measured a photolysis frequency for hexanal in the EUPHORE chamber in Valenica (zenith angle 16.0°, latitude 40°N for 1 July) which give a lifetime for hexanal of approximately 15 h. Similar photolysis rates have also been measured for other long chain aldehydes (http://www.iupac.org/publications/pac/2001/pdf/7303x0487.pdf). Although when averaged over a whole year for different zenith angles, flux densities etc. photolysis will not be as important as OH radical loss it still needs to be discussed. Plagens (2001) have observed cis-trans isomerisation for trans-2-hexenal in EUPHORE with a very slow further photolysis loss indicating that photolysis is probably not so important a loss process for unsaturated aldehydes.

Page 5175 (line 10): in this section on possible heterogeneous chemistry of aldehydes the authors should mention the involvement of aldehydic compounds in the formation of oligomeric components in secondary organic aerosol, e.g. Gao et al. J. Phys Chem A 108 (2004) 10147; Kalberer et al. Science 303 (2004) 1659; Jang et al. Science 298 (2002) 814.

In Table 2 the "Radical" column is not necessary since all the information is for Cl atoms and this is stated in the figure caption.

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Although the use of the English language is fair, the phrasing is sometimes strange and awkward in places and the definite and indefinite articles are often omitted. If the authors have the possibility I would suggest that they have the manuscript read by a native English speaker. This would make for a smoother read and also make their arguments in some instances easier to comprehend.

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