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Referees comments:
Tropospheric photooxidation of CF_3CH_2CHO and $CF_3(CH_2)_2CHO$ initiated by Cl atoms and OH radicals
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General comments:

This paper describes a kinetic study on the reactions of hydroxyl radicals and chlorine atoms with the fluorinated aldehydes CF_3CH_2CHO and $CF_3(CH_2)_2CHO$. Rate coefficient data for the reactions were determined as a function of temperature and pressure using absolute rate techniques. Pulsed laser photolysis was used to generate OH radicals and Cl atoms and they were monitored by laser induced fluorescence and vacuum UV resonance fluorescence respectively. The experiments appear to have been carried out with considerable care and attention to detail, and information concerning individual experimental runs clearly presented. The methods employed to calculate rate parameters from the raw experimental data have been logically presented. The reductions in the rate coefficients for reaction with OH and Cl following replacement of the terminal CH_3- group in aldehydes by a CF_3- group were rationalized in terms of the electron withdrawing effect of the CF_3- group. The kinetic data were used to estimate the atmospheric lifetimes of fluorinated aldehydes and hence the environmental impact of releases of their precursor fluorinated alcohol compounds. The rate coefficients determined at room temperature for the reactions of OH and Cl with CF_3CH_2CHO were compared with those previously reported and found to be in good agreement. This paper should be published with minor corrections.

Specific comments:

(1)
In the OH radical experiments, the concentration of aldehydes was determined from both FTIR and flow rate measurements. It was pointed out that there was a difference of up to 20% in the two different determinations. Since the rate coefficients were derived using the concentration values, a possible explanation for this discrepancy should be given.

(2)
The rate coefficient at 298 K for the reaction of Cl with $CF_3(CH_2)_2CHO$ was found to be around a factor of 2 higher than that for the reaction with CF_3CH_2CHO. However, the reported activation energies for the reactions are about 5 and 2.5 kJ/mole for $CF_3(CH_2)_2CHO$ and CF_3CH_2CHO respectively. The corresponding A factors for the reactions are 29 and 4.4 (in units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). Hence, it appears that internal compensation of the Arrhenius parameters has occurred.

(3)
The available data indicate that reaction of both OH radicals and Cl atoms with aldehydes results in abstraction of the aldehydic hydrogen atom. As expected, fluorine substitution in the aldehydes results in a decrease in reactivity with respect to reaction with the electrophilic OH radicals and Cl atoms. Since the C-H bond strength in the –CHO group is likely to be little changed following fluorine substitution in aldehydes, the reduction in reactivity must be largely associated with the inductive electron withdrawing effect of the CF_3- group. It is of interest to note that the reduction in reactivity is somewhat higher for the Cl atom reactions than for the OH radical reactions. This slight difference may be associated with the difference in the mechanisms for the OH and Cl reactions. Although both the reactions of OH and Cl with

aldehydes result in H atom abstraction, the reactions proceed through different pathways. As discussed by Smith and Ravishankara (2002), the reaction of OH radicals with carbonyl compounds involves the initial formation of a hydrogen-bonded complex between the attacking OH radical and the carbonyl group providing a lower energy pathway for the reaction.. Subsequent decomposition of the complex leads to formation of the final reaction products. It is not possible for the reaction of Cl atoms with the aldehydes to occur by a hydrogen-bonded pathway, and hence this direct hydrogen abstraction pathway may be less facile than the corresponding reaction with OH.

(4)
It is unlikely that releases of fluorinated alcohols will be sufficiently high to influence ozone formation in the troposphere to any significant extent. In a similar manner they will not make a contribution to global warming. The importance of these compounds, and hence the fate of their aldehyde degradation products, is the possibility that they will lead to the formation of fluorinated carboxylic acids.

Technical corrections:

Throughout the text molecule cm^{-3}, not $moleculecm^{-3}$.

Page 24784 line 7 …work for the detection…
line 14 …dependence over the range investigated…
Page 24785 The first sentence is redundant. Leave it out
line 6 …Although HFCs…
Page 24786 line 9 …for these reactions…
Page 24787 line 13 …was first inputted into a fast preamplifier, collected with…
Page 24788 line 2 …A schematic diagram of….
line 20 …Optical measurement of…
line 27 …which were…
Page 24789 line 13 …In some experiments the…
Page 24790 line 21 …in large excess with respect…
Page 24793 line 6 …2 x 10^{16} molecule…
Page 24797 line 7 …one day across the…
line 8 …The value of τ_{Cl}…
line 14 …atoms are responsible for the…
line 23 …aldehyde increases with decreasing pressure, the…
Page 24798 line 1 …process across the….
line 2 …Little information…
line 5 …Henry's law coefficients for some…
line 13 …aldehydes have not…
line 20 …negligible compared to…
line 21 …radicals will be..
line 22 …may significantly influence air quality…..
line 27 …yielding the formyl radical (HCO) and a fluoroalkyl radical…
line 28 …Further reactions of all…
line 29 …degradation processes may make a slight contribution to ozone formation.
Page 24799 line 1 …The role of Cl reactions in ozone formation should also be….
line 16 …and k_{OH} for reactions with CF_3CH_2CHO and $CF_3(CH_2)_2CHO$ in the…
line 25 …to favour H-atom abstraction…
line 27 …This implies….
Page 24800 line 1 …contribute to air pollution.