Telomer Research Program

Report Title: Extended Laboratory Study of the Atmospheric Degradation of Fluorinated Alcohols

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Study Objective

The project goal was the determination of the photolysis rate of perfluorinated aldehydes, $C_6F_{13}CHO$ and $C_8F_{17}CHO$, produced in the OH-initiated oxidation of the corresponding Telomer B Alcohols, $C_6F_{13}CH_2CH_2OH$ and $C_8F_{17}CH_2CH_2OH$. These data are important since atmospheric photolysis of these aldehydes may compete with reaction with OH radicals, thereby reducing or even eliminating production of the corresponding perfluorocarboxylic acids, in low NO_x conditions.

Materials and Methods

All the photolysis experiments using solar radiation were performed at the outdoor European reactor EUPHORE in Valencia, Spain. The EUPHORE facility consists of two independent hemispherical outdoor simulation chambers, made of FEP foil, with a volume of 200 m^3 each (http://www.gva.es./ceam). EUPHORE has a variety of instruments (including FTIR, GC-FID, HPLC) available for in-situ analysis or off-line sampling and the high FTIR detection sensitivity allows use of VOC and NO_X concentration ranges close to those present in the atmosphere.

Since the perfluorinated aldehydes were not (and are not) available, the experimental design was to produce perfluorinated aldehydes indirectly in the EUPHORE chamber via the OH-initiated oxidation of the corresponding Telomer B Alcohols. This approach met with difficulties and additional experiments were also carried out at EUPHORE using Cl-initiated oxidation of $C_6F_{13}CH_2OH$ in air to directly produce $C_6F_{13}CHO$. In addition, experiments have been carried out on the Cl-initiated oxidation of $C_6F_{13}CH_2OH$ in air using the 480L glass photoreactor at the University of Wuppertal.

Research grade samples of the Telomer B Alcohols and $C_6F_{13}CH_2OH$ are readily available. OH radicals were produced in-situ by photolysis of HONO or H_2O_2. Cl atoms were produced by photolysis of ClC(O)C(O)Cl at EUPHORE and by photolysis of molecular Chlorine at Wuppertal. All chemicals used were lab grade reagents.

At EUPHORE, molecular species concentrations and product analysis were monitored by long-path length FTIR and GC-MS and photolysis experiments were performed used natural light. At Wuppertal, experiments were performed in a 480L duran glass reactor interfaced to an in-situ FTIR spectrometer (Nicolet Magna 520) with a pathlength of 51.6 m and a resolution of 1 cm^{-1}. The reactor was surrounded with 20 superactinic lamps (Philips TLA 40W/05, $300 < \lambda < 450$ nm, $\lambda_{max} = 360$ nm) used to photochemically initiate the experiments.

Findings

OH-initiated oxidation of $C_6F_{13}CH_2CH_2OH$ (June 28th at EUPHORE)

The experiment was performed using the photolysis of HONO as OH radical source and the initial concentration of $C_6F_{13}CH_2CH_2OH$ was 250 ppbv. The loss of $C_6F_{13}CH_2CH_2OH$ in absence of light was found to be comparable to that due to dilution (corresponding to the loss of SF_6) indicating that the wall loss of $C_6F_{13}CH_2CH_2OH$ is negligible in our experimental conditions.

During the experiment, the consumption of $C_6F_{13}CH_2CH_2OH$ due to its reaction with OH radicals was estimated to be around 16 %. GC-MS analysis showed two main products of the reaction. These products could not be not positively identified, however, one of them may be the Telomer aldehyde ($C_6F_{13}CH_2CHO$). The FTIR analysis was rapidly complicated following the formation of the reaction products and the overlap of the fluorinated compounds with similar IR spectra. However, the IR spectra obtained during the experiments showed the presence of an unidentified band 1194-1264 cm^{-1} which could not be attributed to CF_2O nor to $C_6F_{13}C(O)H$ (see Figure 1).

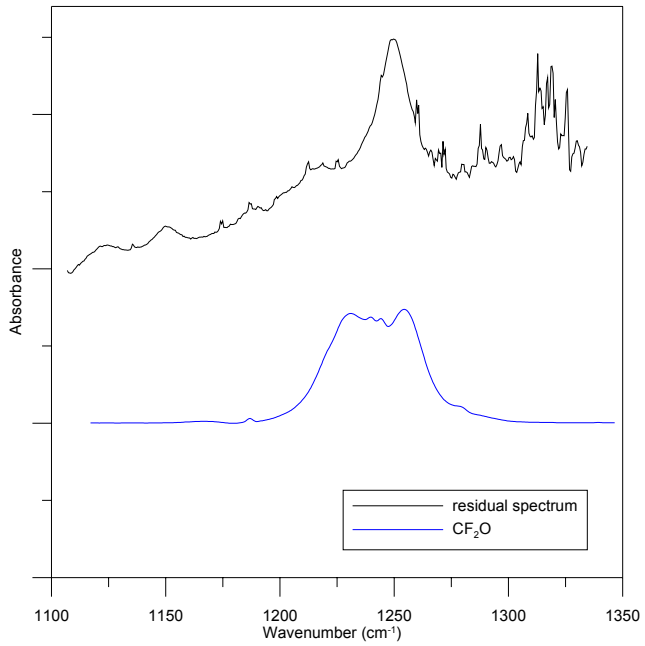

Figure 1: Residual spectrum after subtraction of $C_6F_{13}CH_2CH_2OH$ and CF_2O

OH-initiated oxidation of $C_8F_{17}CH_2CH_2OH$ (June 29th and 30th at EUPHORE)

Two runs were performed: in the first one the photolysis of HONO was used as the OH source while H_2O_2 was used in the second one. The $C_8F_{17}CH_2CH_2OH$ initial concentrations were 130 ppbv and 180 ppbv, respectively.

In both experiments the consumption of $C_8F_{17}CH_2CH_2OH$ was estimated to be 20 %. GC-MS analysis showed two main products, one of them may be the "first" aldehyde $C_8F_{17}CH_2CHO$ which was supported by HPLC-MS analysis that indicated the formation of a carbonyl compound. Figure 2 shows the concentration-time profile of $C_8F_{17}CH_2CH_2OH$.

Similarly to what was observed for $C_6F_{13}CH_2CH_2OH$, the FTIR analysis was rapidly complicated by the overlapping IR bands of different fluorinated compounds present in the system (reactant and reaction products). **Hence, in absence of IR spectra of pure product samples and reference spectra, it is still difficult to conclusively identify the reaction products.**

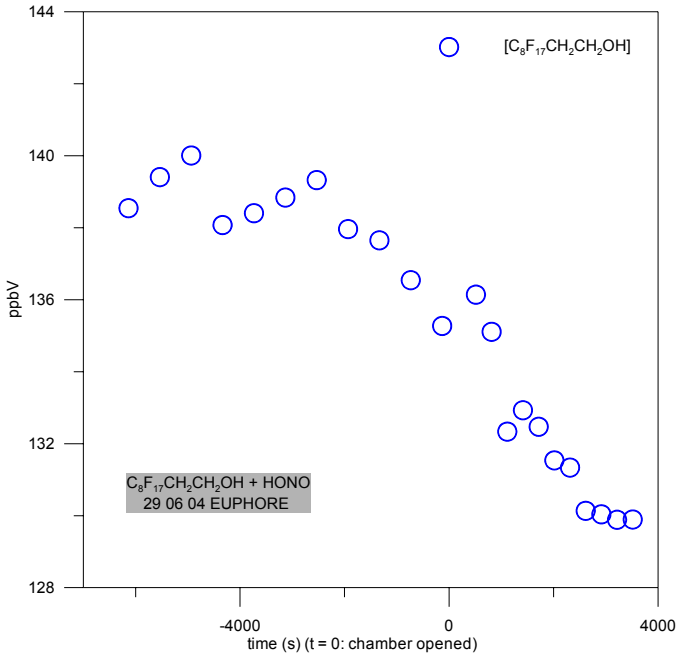

Figure 2

Cl-Initiated oxidation of $C_6F_{13}CH_2OH$ at EUPHORE (July 1st and 2nd)

The aim of these experiments was to generate $C_6F_{13}CHO$ directly and check for its photolysis under sunlight conditions.

Chlorine atoms were produced using the photolysis of ClC(O)C(O)Cl. Initial concentrations of $C_6F_{13}CH_2OH$ were 180 ppbv and 220 ppbv, respectively on July 1st and 2nd. The initial concentrations of ClC(O)C(O)Cl were chosen in order to obtain different consumption of $C_6F_{13}CH_2OH$ in both experiments (85 % and 15 % in the first and second run, respectively).

In both experiments, CF_2O was the major product observed by FTIR analysis (see Figure 3).

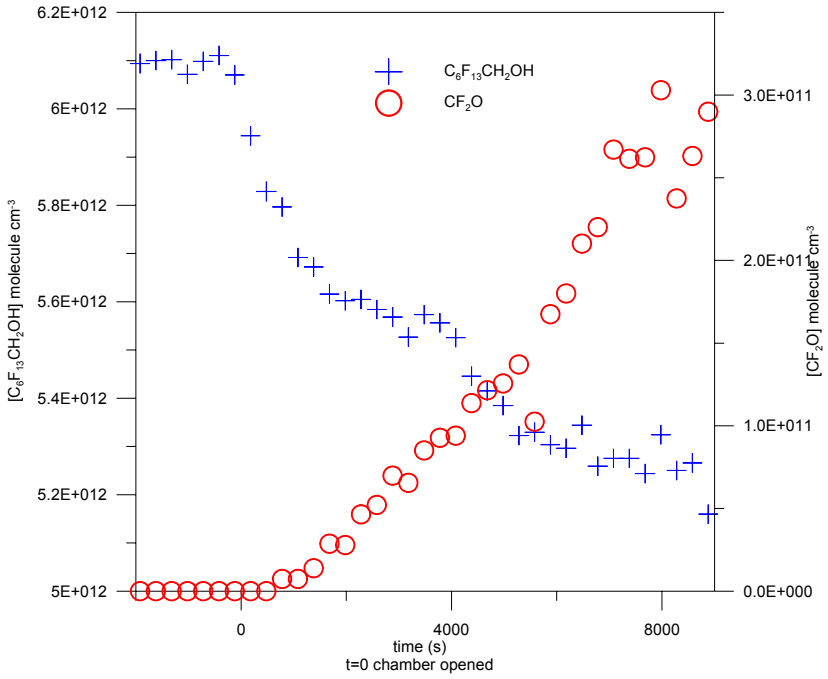

Figure 3: Concentration-time profiles of $C_6F_{13}CH_2OH$ and CF_2O.

The expected mechanism of the Cl-initiated oxidation of $C_6F_{13}CH_2OH$ leading to the aldehyde $C_6F_{13}CHO$ is:

$$Cl + C_6F_{13}CH_2OH \rightarrow HCl + C_6F_{13}CHOH$$

$$C_6F_{13}CHOH + O_2 \rightarrow C_6F_{13}CHO + HO_2$$

$C_6F_{13}CHO$ then reacts with Cl and could also be photolysed:

$$C_6F_{13}CHO + Cl \rightarrow C_6F_{13}CO + HCl$$

$$C_6F_{13}CHO + h\nu \rightarrow C_6F_{13}CO + H$$

$$C_6F_{13}CHO + h\nu \rightarrow C_6F_{13} + HCO$$

$C_6F_{13}CO$ and C_6F_{13} radicals will ultimately lead to CF_2O.

The rate constants obtained at Wuppertal for ($k(Cl + C_6F_{13}CH_2OH)$ and $k(Cl + C_6F_{13}CHO)$) (see next section) were used to fit the EUPHORE experimental profiles to tentatively assess the importance of the photolysis of the aldehyde. **Again, no definitive conclusion could be drawn because the FTIR analysis was rapidly complicated following the formation of the reaction products and the overlapping of the fluorinated compounds with similar IR spectra.**

Kinetics & mechanism of the Cl reaction with $C_6F_{13}CH_2OH$ studied at Wuppertal

The relative rate technique was used to measure the rate constant of the reaction of Cl with $C_6F_{13}CH_2OH$ relative to that of Cl with CH_3Cl.

The relevant reactions in the system were:

$$Cl + C_6F_{13}CH_2OH \rightarrow \text{products} \qquad (1)$$

$$Cl + CH_3Cl \rightarrow \text{products} \qquad (2)$$

Assuming that the fluoroalcohol and the CH_3Cl are consumed only by Cl, it can be shown that:

$$\ln([C_6F_{13}CH_2OH]_o/([C_6F_{13}CH_2OH]_t)/ = k_1/k_2 \ln([CH_3Cl]_o/([CH_3Cl]_t)$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t, respectively.

Reactants concentrations were monitored using the IR absorption features 3550-3650 cm^{-1} and 2820-3150 cm^{-1} for $C_6F_{13}CH_2OH$ and CH_3Cl, respectively. Infrared spectra were derived from 32 co-added interferograms. Control experiments showed that side reactions such as photolysis of $C_6F_{13}CH_2OH$ and CH_3Cl, as well as heterogenous and dark reactions were negligible in our experimental conditions.

Using the value of $k(Cl+CH_3Cl) = 4.8x10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for the reference reaction, we have derived the reaction rate constant of Cl with $C_6F_{13}CH_2OH$:

$$\mathbf{k\ (Cl + C_6F_{13}CH_2OH) = (6.5 \pm 0.4)\ x10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}}$$

In Table 1, we have compared this rate constant with the data reported previously for the reactions of Cl with shorter fluorinated alcohols with the formula $C_nF_{2n+1}CH_2OH$ as shown. The length of C_nF_{2n+1} group does not effect the reactivity of Cl atoms with $C_nF_{2n+1}CH_2OH$ ($k(Cl+C_nF_{2n+1}CH_2OH) \approx 6.5x10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for n = 1 up to n = 6).

Table 1: Rate constant values for the reaction of Cl with fluoroalcohols

Fluoroalcohol	**k(Cl)**
CF_3CH_2OH	$(6.5 \pm 0.5)\ x10^{-13}$
$CF_3CF_2CH_2OH$	$(6.5 \pm 0.5)\ x10^{-13}$
$CF_3(CF_2)_2CH_2OH$	$(6.5 \pm 0.5)\ x10^{-13}$
$CF_3(CF_2)_3CH_2OH$	$(6.5 \pm 0.5)\ x10^{-13}$
$CF_3(CF_2)_5CH_2OH$	$(6.5 \pm 0.4)\ x10^{-13}$

Product Study of the Cl reaction with $C_6F_{13}CH_2OH$:

The Cl-initiated oxidation of $C_6F_{13}CH_2OH$ was investigated using the same system as that used for the kinetic study. The reaction of Cl with $C_6F_{13}CH_2OH$ proceeds by abstraction of H-atom from $–CH_2-$ group followed by reaction with O_2 leading to the perfluorinated aldehyde $C_6F_{13}CHO$, as already mentioned :

$$Cl + C_6F_{13}CH_2OH \rightarrow C_6F_{13}CHOH + HCl$$

$$C_6F_{13}CHOH + O_2 \rightarrow C_6F_{13}CHO + HO_2$$

The aldehyde may undergo further reaction with Cl atoms leading to other fluorinated compounds as end products.

Figure 4 shows an example of the experimental concentration profile of $C_6F_{13}CHO$ versus $C_6F_{13}CH_2OH$.

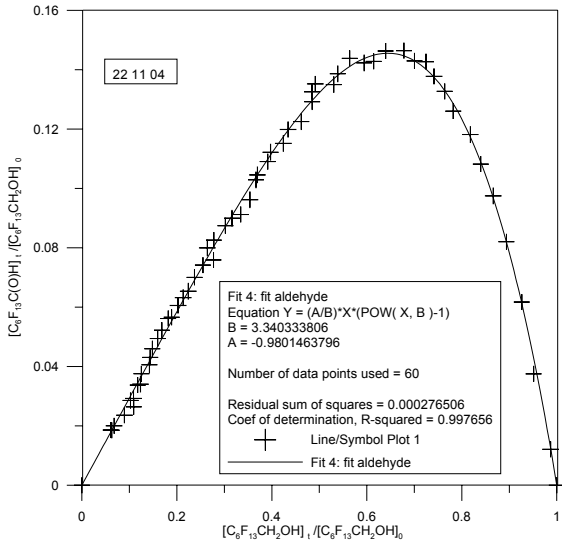

Figure 4: Formation of $C_6F_{13}CHO$ versus loss of $C_6F_{13}CH_2OH$

The reaction rate constant of Cl with $C_6F_{13}CHO$ was derived by fitting these profiles:

$$\mathbf{k(Cl + C_6F_{13}CHO) = (2.8 \pm 0.7)x10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}}$$

Conclusion

The reaction of $C_6F_{13}CH_2CH_2OH$ with OH radicals produces two main products. These products could not be not positively identified, however, one will likely be the Telomer aldehyde ($C_6F_{13}CH_2CHO$). Similarly the reaction of $C_8F_{17}CH_2CH_2OH$ with OH radicals produces two main products. GC-MS analysis showed two main products, one of them may be the "first" aldehyde $C_8F_{17}CH_2CHO$ which was supported by HPLC-MS analysis that indicated the formation of a carbonyl compound.

The Cl-Initiated oxidation of $C_6F_{13}CH_2OH$ was used to generate $C_6F_{13}CHO$ directly and check for its photolysis under sunlight conditions. Large conversion of the alcohol (up to 85%) was observed and CF_2O was the major product observed by FTIR analysis. Experimental rate constants obtained at Wuppertal were used to fit the EUPHORE experimental profiles to tentatively assess the importance of the photolysis of the aldehyde but no definitive conclusions could be drawn..

At Wuppertal, the rate constant of the reaction of Cl with $C_6F_{13}CH_2OH$ relative to that of Cl with CH_3Cl was measured.

Using the value of $k(Cl+CH_3Cl) = 4.8x10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for the reference reaction, we have derived the reaction rate constant of Cl with $C_6F_{13}CH_2OH$:

$$\mathbf{k\ (Cl + C_6F_{13}CH_2OH) = (6.5 \pm 0.4)\ x10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}}$$

In addition, the reaction rate constant of Cl with $C_6F_{13}CHO$ was derived:

$$\mathbf{k(Cl + C_6F_{13}CHO) = (2.8 \pm 0.7)x10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}}$$

Unfortunately, the experiments performed at EUPHORE and in Wuppertal are inconclusive. Due to the absence of spectra of pure sample of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CHO$, it was not possible to quantify the formation of these two aldehydes during the experiments. Other experiments are planned in the near future at EUPHORE to look directly at the photolysis of shorter aldehydes (C_3F_7CHO and C_4F_9CHO) which are available commercially through their corresponding hydrates. A few tests have been already conducted on C_3F_7CHO using an indoor smog chamber.

Publications / Presentations

T. KELLY, V. BOSSOUTROT, I. MAGNERON, K. WIRTZ, J. TREACY, A. MELLOUKI, H. SIDEBOTTOM, G. LE BRAS
A kinetic and mechanistic study of the reactions of OH radicals and Cl atoms with 3,3,3-trifluoropropanol under atmospheric conditions
J. Phys. Chem. A (2005) 7, 334-341

A MELLOUKI, G. SOLIGNAC, G. LE BRAS, I. BARNES, R.L. WATERLAND
The atmospheric chemistry of n-$C_6F_{13}CH_2OH$
To be presented at the SETAC Europe 15th Annual Meeting, Lille, 22-26 May 2005.
(This work will also be submitted for publication)