Supplementary Information

Atmospheric Sink of Chlorofluoroacetates: Temperature Dependent Rate Coefficients, Product Distribution of their Reactions with Cl Atoms and $CF_2ClC(O)OH$ Formation

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Content Summary

Kinetic data plots for the reactions of methyl chlorodifluoroacetate and ethyl chlorodifluoroacetate with Cl atoms obtained at 287, 303 and 313 K, using chloromethane as reference hydrocarbon, Figure S1 and S2, respectively.

Concentration-time profiles for the reaction of Cl with MCDFA and ECDFA, Figure S3 and S6, respectively.

Yield plots for the products formed from the reaction of Cl with MCDFA (Figure S4) and for Cl + ECDFA reaction (Figure S7). IR spectra plots used in the identification of the products formed in the reaction of Cl with ECDFA (Figure S5).

Comparison of the residual product IR spectrum (panel A) obtained from experiments performed on the reaction of Cl with MCDFA with a computed IR spectrum (panel B) for the expected major product $CF_2ClC(O)OC(O)H$ (Figure S8). A list of the concentrations, number of experiments performed, infrared absorption frequencies and chemicals used with purities is given.

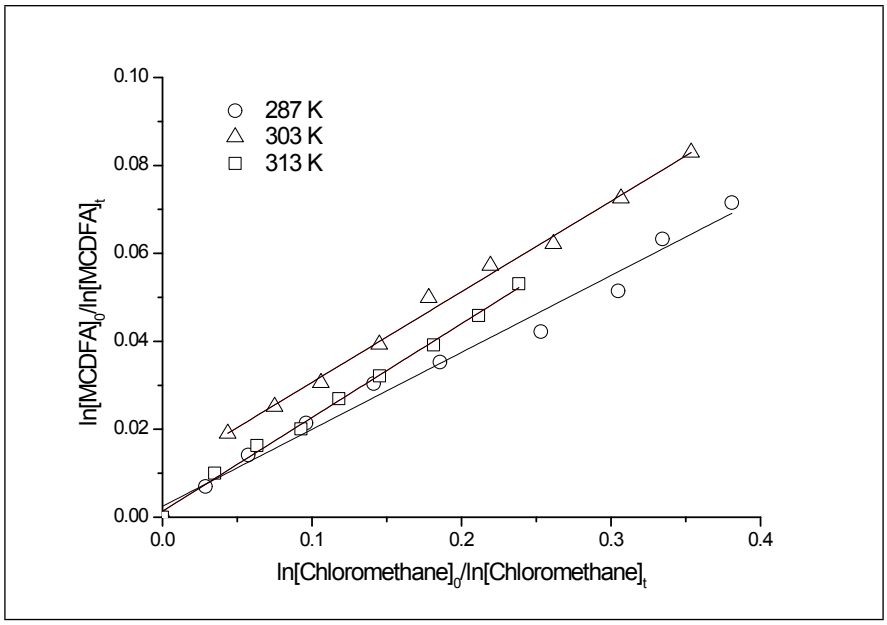

Figure S1: Plot of the kinetic data for the reaction of methyl chlorodifluoroacetate with Cl atoms obtained at 287, 303 and 313 K, using chloromethane as reference hydrocarbon.

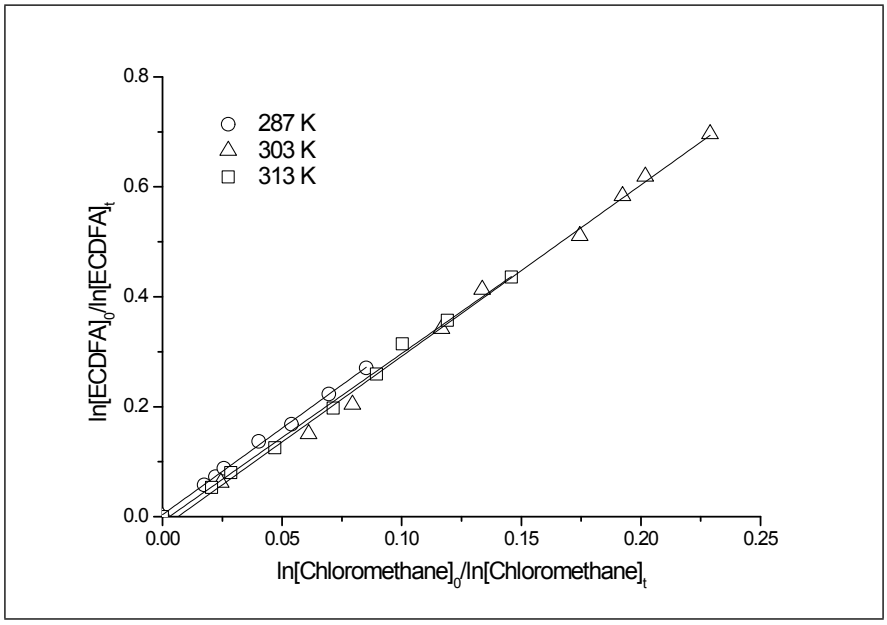

Figure S2: Plot of the kinetic data for the reaction of ethyl chlorodifluoroacetate with Cl atoms obtained at 287, 303 and 313 K, using chloromethane as reference hydrocarbon.

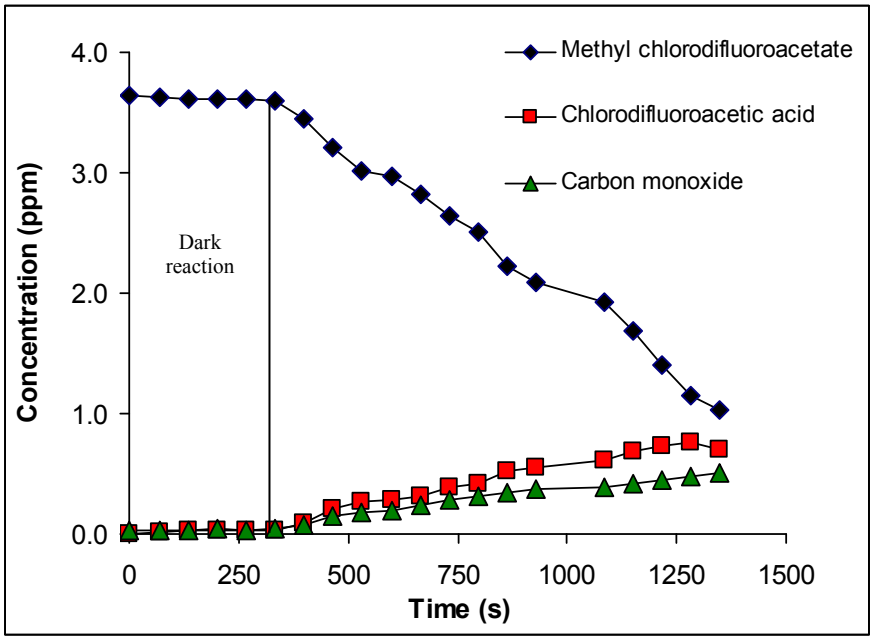

Figure S3: Concentration-time profiles of methyl chlorodifluoro acetate (MCDFA) and the reaction products chlorodifluoroacetic acid and carbon monoxide obtained from the irradiation of a MCDFA/Cl_2/air reaction mixture.

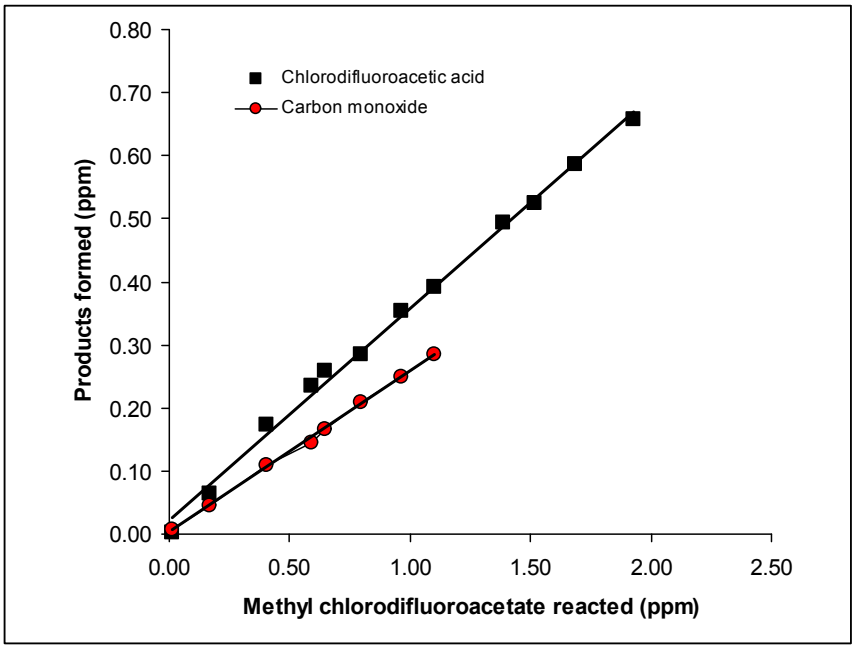

Figure S4: Plots of the concentrations of the reaction products chlorodifluoroacetic acid and carbon monoxide as a function of reacted methyl chlorodifluoroacetate obtained from the irradiation of a MCDFA/Cl_2/air reaction mixture.

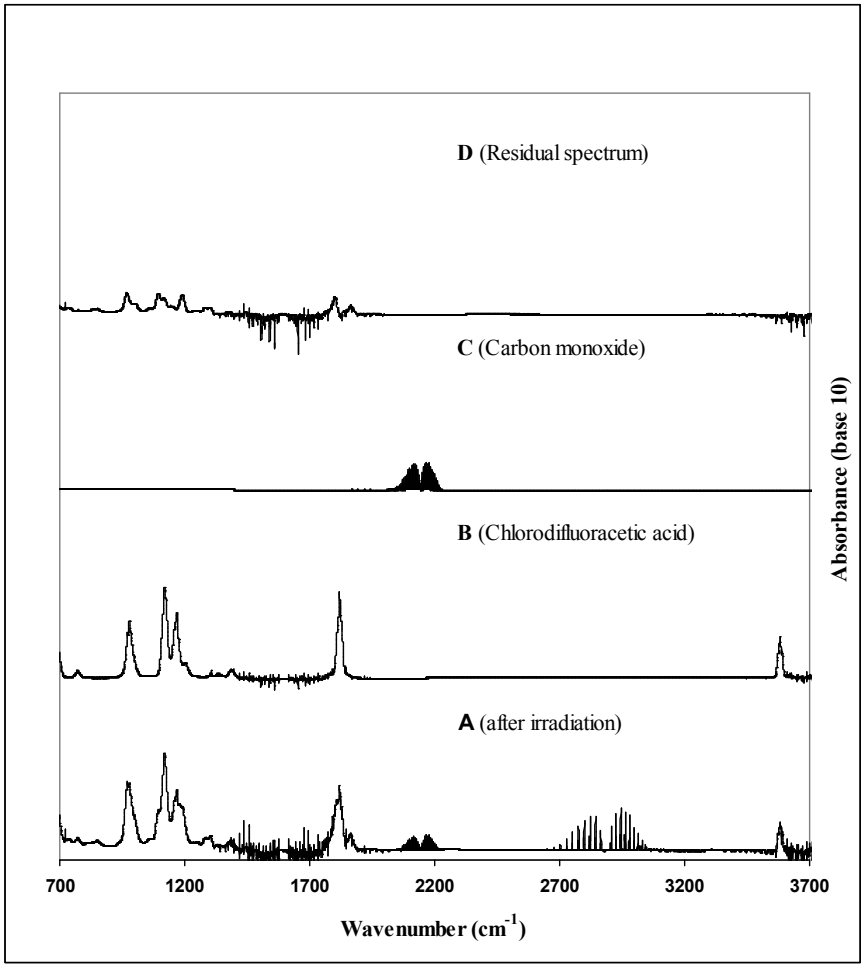

Figure S5: Trace A shows the infrared spectrum of ECDFA/Cl_2/air reaction mixture after irradiation and subtraction of residual ethyl chlorodifluoroacetate. Trace B shows a reference spectrum of chlorodifluoroacetic acid. Trace C shows a reference spectrum of carbon monoxide and trace D shows the residual product spectrum obtained after subtraction of features due to the products identified (traces B and C) from the spectrum in trace A.

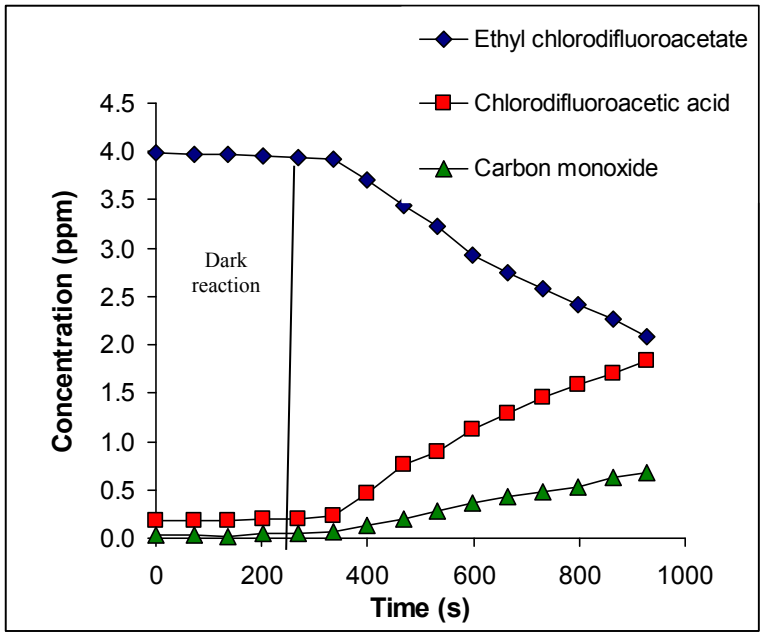

Figure S6: Concentration-time profiles of ethyl chlorodifluoroacetate (ECDFA) and the reaction products chlorodifluoroacetic acid and carbon monoxide obtained from the irradiation of an ECDFA/Cl_2/air reaction mixture.

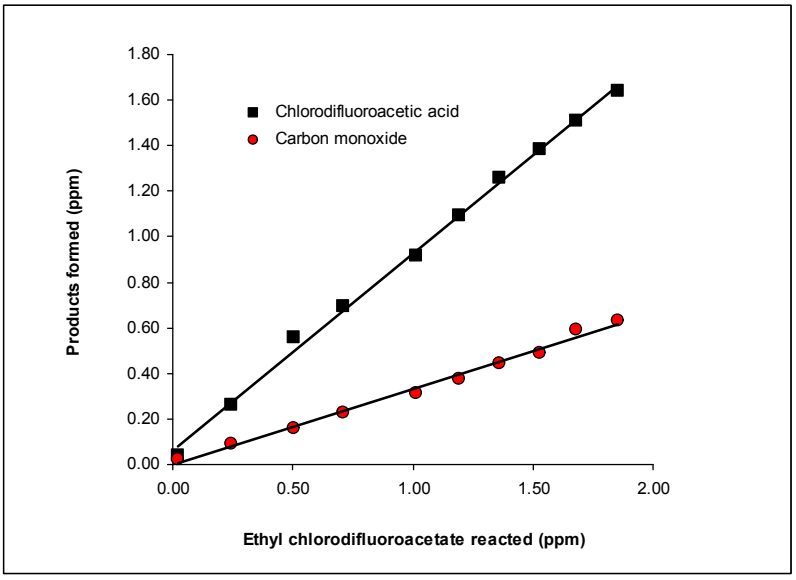

Figure S7: Plots of the concentrations of the reaction products chlorodifluoroacetic acid and carbon monoxide as a function of reacted ethyl chlorodifluoroacetate obtained from the irradiation of a ECDFA/Cl_2/air reaction mixture.

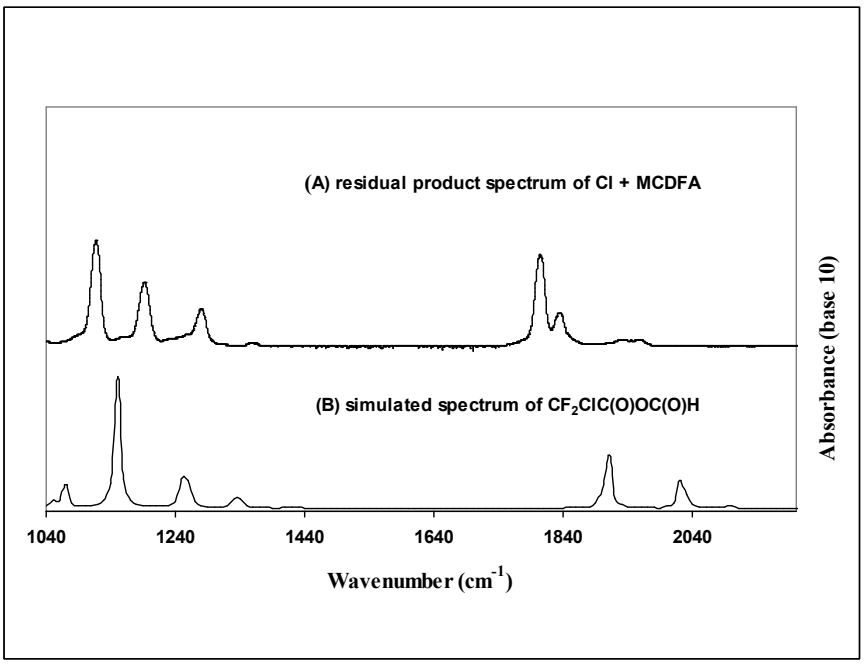

Figure S8: Comparison of the residual product IR spectrum (panel A) obtained from experiments performed on the reaction of Cl with MCDFA with a computed IR spectrum (panel B) for the expected major product $CF_2ClC(O)OC(O)H$.

Table S1: Removal rates of the unsaturated esters studied as a function of altitude in the troposphere.

Altitute (Km)	T(K)	$k_{Cl+MCDFA}(T)[Cl]$ (s^{-1})	$k_{Cl+ECDFA}(T)[Cl]$ (s^{-1})
0	298.15	9.93×10^{-10}	1.55×10^{-8}
1	291.65	8.97×10^{-10}	1.43×10^{-8}
2	285.15	8.06×10^{-10}	1.31×10^{-8}
3	278.65	7.21×10^{-10}	1.20×10^{-8}
4	272.15	6.42×10^{-10}	1.09×10^{-8}
5	265.65	5.68×10^{-10}	9.87×10^{-9}
6	259.15	4.99×10^{-10}	8.89×10^{-9}
7	252.65	4.36×10^{-10}	7.96×10^{-9}
8	246.15	3.78×10^{-10}	7.09×10^{-9}
9	239.65	3.25×10^{-10}	6.27×10^{-9}
10	233.15	2.78×10^{-10}	5.51×10^{-9}

Concentrations, number of experiments performed, infrared absorption frequencies and chemicals used

The following typical initial concentrations in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) were used for the chlorofluoroesters and the reference compound in the experiments: (0.27-0.41) ppmV for methyl chlorodifluoroacetate; (0.25-0.54) ppmV for ethyl chlorodifluoroacetate; and (0.42-0.64) ppmV for chloromethane. The initial concentration of Cl_2 was typically around 5 ppmV.

For the kinetics results, we have performed three or four runs of the each reaction studied at each temperature. In addition, for the products studies we did four experiments for each reaction.

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): methyl chlorodifluoroacetate at 1315 and 1193; ethyl chlorodifluoroacetate at 1311 and 1188; and chloromethane at 3096 and 3071. The wavelength precision of the detection system (FTIR Nicolet) is better than 0.01 cm^{-1}.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), methyl chlorodifluoroacetate (Aldrich, 99%), ethyl chlorodifluoroacetate (Aldrich, 99%), chloromethane (Messer Griesheim 99 %) and Cl_2 (Messer Griesheim, 2.8).