Supporting Information for

Atmospheric chemistry of *(Z)*-$CF_3CH=CHCl$: Products and mechanisms of the Cl atom, OH radical and O_3 reactions, and role of *(E)-(Z)* isomerization

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Section 1: Products of the Cl atom initiated oxidation of (*Z*)-$CF_3CH=CHCl$

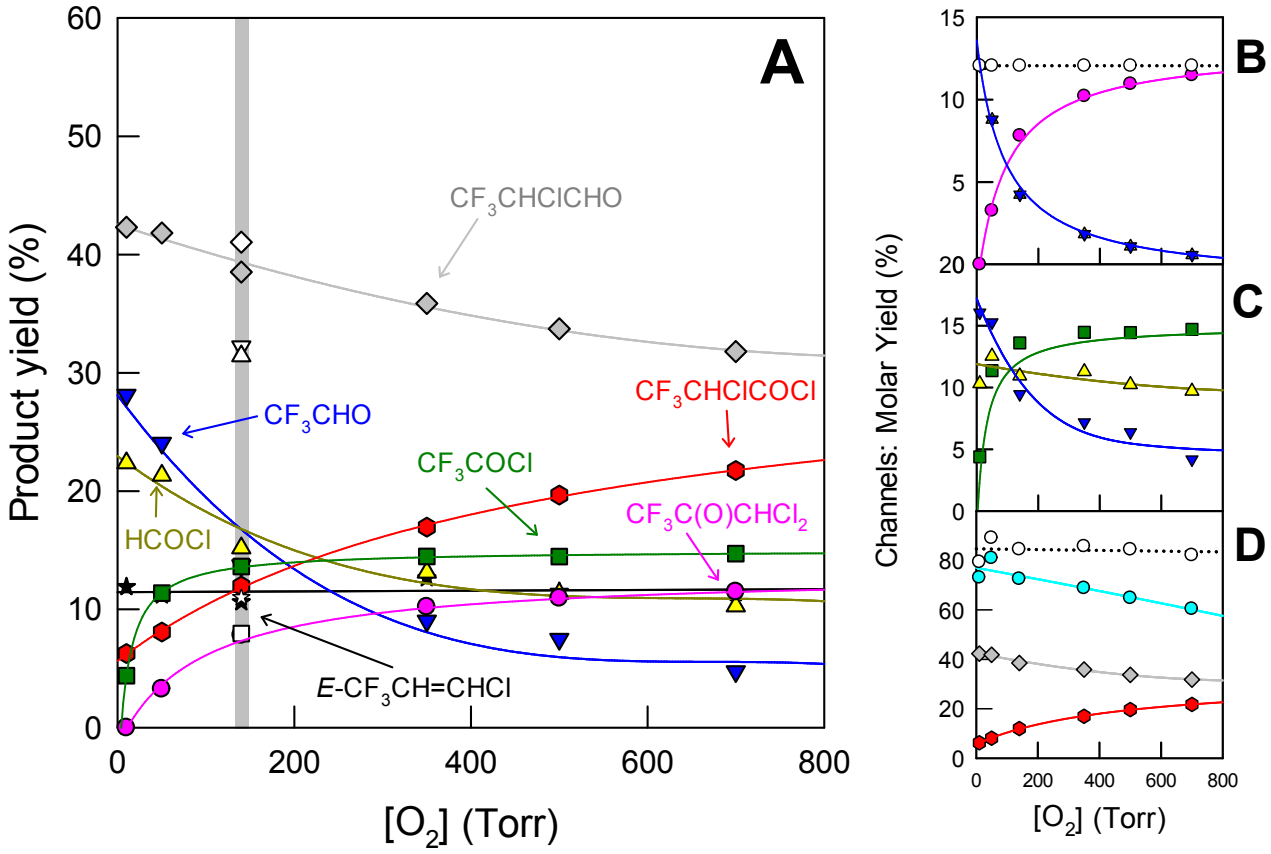

Figure S1: Panel A: Observed molar yield of HCOCl (triangles), CF_3COCl (squares), CF_3CHO (inverted triangles), *(E)*-$CF_3CH=CHCl$ (stars), $CF_3CHClCHO$ (diamonds), $CF_3CHClCOCl$ (hexagons), and $CF_3C(O)CHCl_2$ (circles) versus the O_2 partial pressure following UV irradiation of *(Z)*-$CF_3CH=CHCl/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure, in the absence (solid symbols) and presence (open symbols) of NO_x. The grey bar serves to highlight the product yields obtained in one atmosphere of air (140 Torr O_2 partial pressure). The line through the *(E)*-$CF_3CH=CHCl$ data is a linear fit. The curves through the HCOCl, CF_3CHO, and $CF_3CHClCHO$ data are polynomial fits to aid visual inspection of the data trends. The line through the CF_3COCl, $CF_3C(O)CHCl_2$, $CF_3CHClCOCl$ data are fits using expressions analogous to those utilized for *E*-$CF_3CH=CHCl$ and described in detail in Sulbaek Andersen *et al.*[1] Panel A-D correspond to the grouping of reaction pathways indicated in the proposed isomer-generic mechanism in Figure 5 of Sulbaek Andersen et al.[1] Panel B: Yield of $CF_3C(O)CHCl_2$ and the corresponding yields of CF_3CHO and HCOCl as a function of $[O_2]$. The sum of the yields is shown as open circles. Panel C: Yield of CF_3COCl together with the residual amount of CF_3CHO and HCOCl as a function of $[O_2]$. Panel D: Yields of $CF_3CHClCOCl$, $CF_3CHClCHO$, the sum of the decomposition channels (light blue circles), and the sum decomposition channels + $CF_3CHClCOCl$ (open circles) as a function of $[O_2]$.

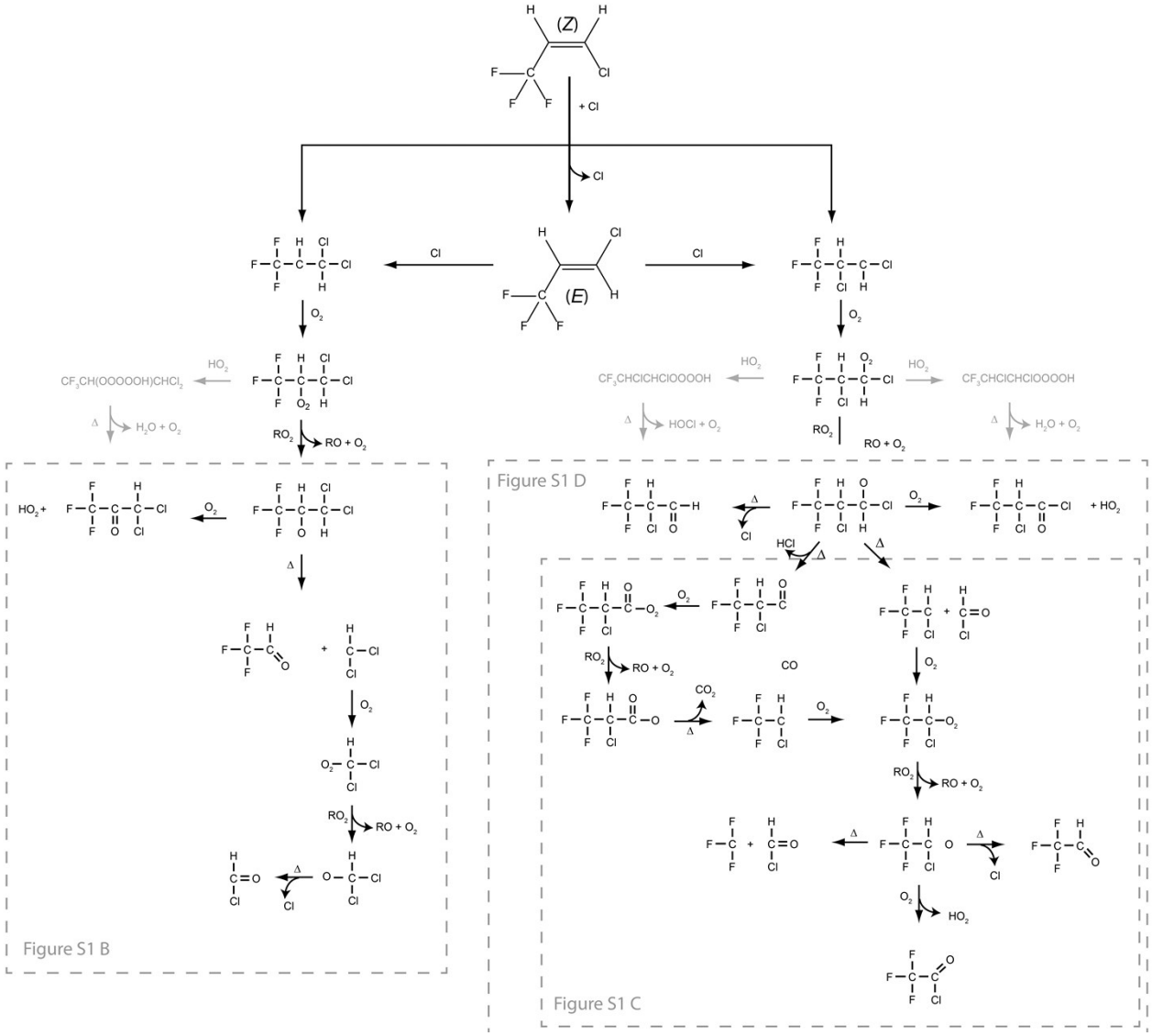

Figure S2: Proposed oxidation mechanism based Sulbaek Andersen et al. [1], and adapted here for the Cl atom initiated oxidation of *Z*-$CF_3CH{=}CHCl$. Dashed boxes include reactions for which oxygen dependencies are illustrated in Figures S1 B through D.

Section 2: Products of the O_3 initiated oxidation of *(E)*-$CF_3CH=CHCl$

The products of reaction (1) were studied by exposing *(E)*-$CF_3CH=CHCl$ to O_3 in excess in the reaction chamber at Ford.

O_3 + *(E)*-$CF_3CH=CHCl \rightarrow$ products (1)

An OH radical scavenger (cyclohexane) was added to the reaction mixtures to avoid potential problems associated with the loss of *(E)*-$CF_3CH=CHCl$ via reaction with OH radicals formed in reaction (1). Initial concentrations of reactants at Copenhagen were 6.9-14.2 mTorr *(E)*-$CF_3CH=CHCl$, 15.6-20.3 mTorr cyclohexane, and 3.42-4.36 Torr O_3 in 700 Torr of air diluent. Initial concentrations of reactants at Ford were 5.9-6.3 mTorr *(E)*-$CF_3CH=CHCl$, 14.0-30.6 mTorr cyclohexane, and 414-2070 mTorr O_3 in 700 Torr of air diluent. Variation of the [cyclohexane] / [*(E)*-$CF_3CH=CHCl$] ratio over the range 2.2-5.2 had no discernable effect on the observed decay of *(E)*-$CF_3CH=CHCl$ suggesting that loss via reaction with OH radicals is not a significant complication. Figure S3 shows the formation of products HCOCl, CF_3CHO and CF_3OH/COF_2. The lines in Figure S3 are linear least squares fit to the data giving yields of (63 ± 9)%, (33 ± 3)%, and (34 ± 4)%, for HCOCl, CF_3CHO and CF_3OH/COF_2 (sum), respectively. See the main text for discussion and comparison with the analogous *(Z)*-$CF_3CH=CHCl$ experiment.

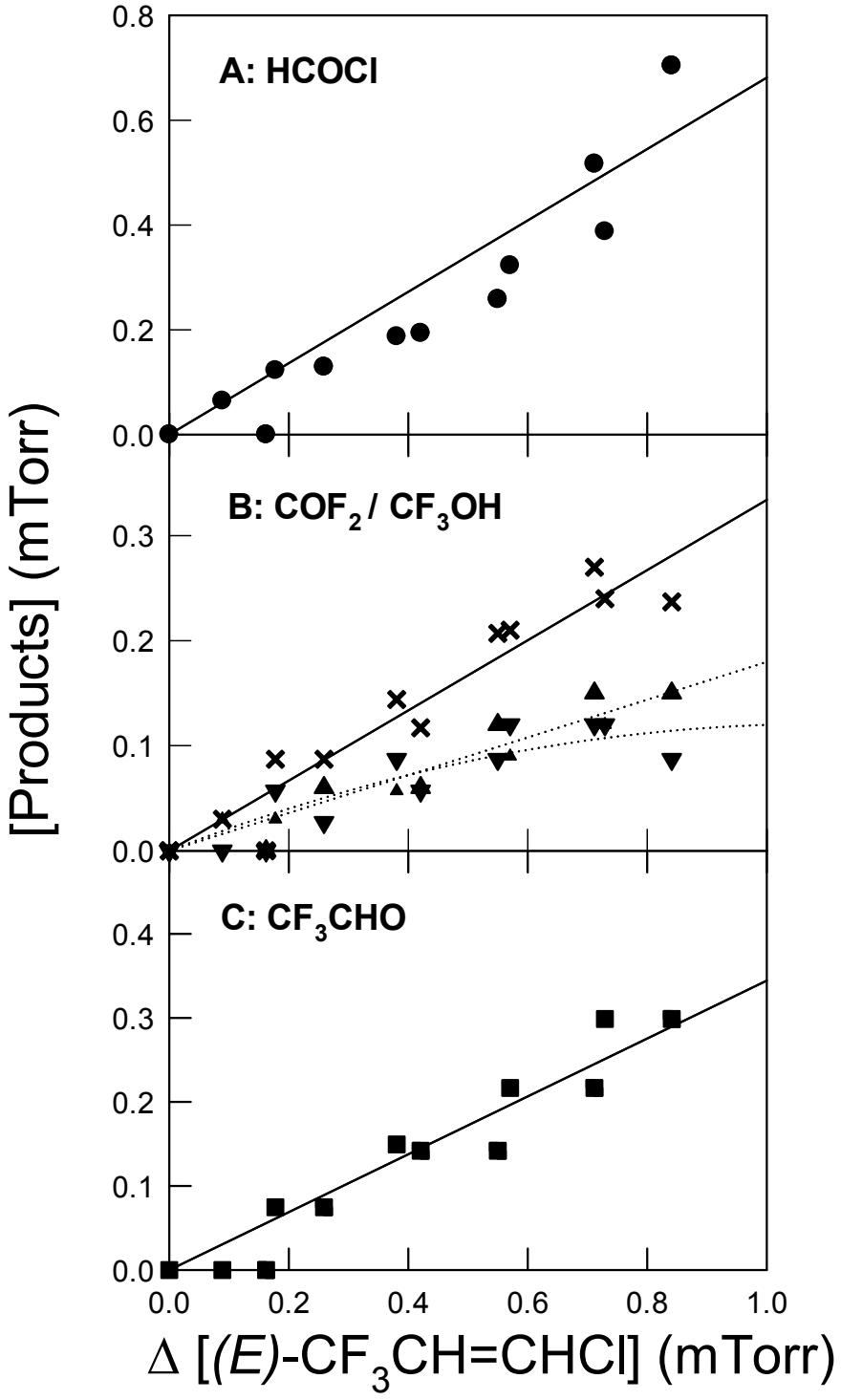

Figure S3: Yields of HCOCl (panel A), COF_2, CF_3OH (panel B), and CF_3CHO (panel C) following the O_3 initiated oxidation of *E*-$CF_3CHCHCl$. Panel B shows a both COF_2 (upwards triangles) and CF_3OH (downwards triangles) as well as the sum of the two compounds (cross marks).

References

[1] M.P.S. Andersen, O.J. Nielsen, M.D. Hurley and T.J. Wallington, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1735-1748.