Supplementary Information

for

Tropospheric chemical degradation of vinyl and allyl acetate initiated by Cl atoms under high and low NO_x conditions

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Content Summary

Concentration-time profiles in the presence and absence of NO_x for the reaction of Cl with VA, Figures S1 and S4, respectively and for the reaction Cl with AA in the presence of NO_x, Figure S6. Yield plots for the products formed from the reaction of Cl with VA in the presence of NO_x (Figure S2) and for the reaction of Cl with AA in the presence of NO_x (Figure S7). IR spectra plots used in the identification of the products formed in the reaction of Cl with VA in the absence of NO_x (Figure S3), AA in the presence of NO_x (Figure S5) and AA in the absence of NO_x (Figure S8). A list of the concentrations, infrared absorption frequencies and chemicals used with purities is given.

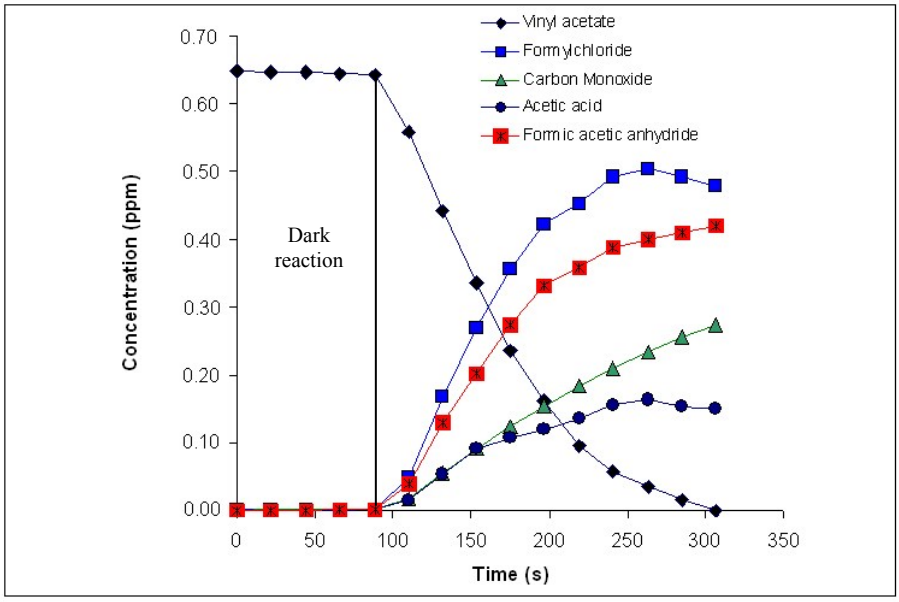

Figure S1: Concentration-time profiles of vinyl acetate (VA) and the reaction products formyl chloride, carbon monoxide acetic acid and formic acetic anhydride obtained from the irradiation of a VA/Cl_2/NO/air reaction mixture.

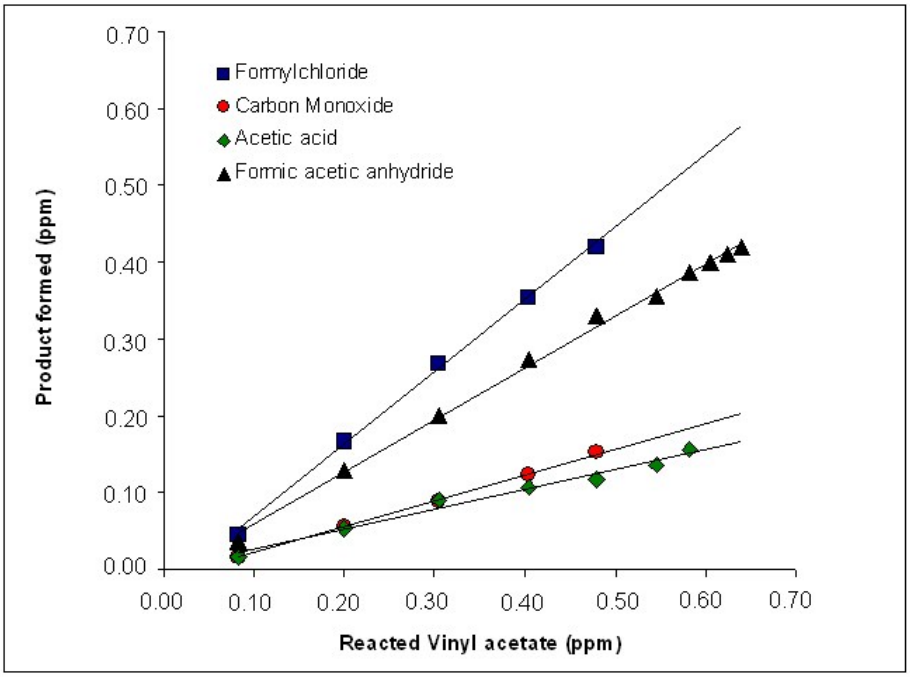

Figure S2: Plots of the concentrations of the reaction products formyl chloride, carbon monoxide, acetic acid and formic acetic anhydride as a function of reacted vinyl acetate obtained from the irradiation of a VA/Cl_2/NO/air reaction mixture.

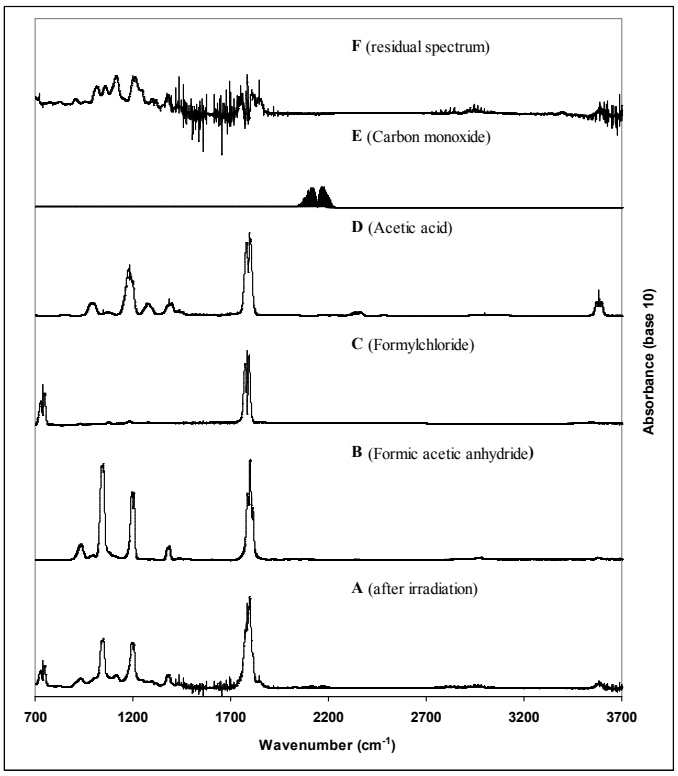

Figure S3: Panel A shows the infrared spectrum of VA/Cl_2/air reaction mixture after irradiation and subtraction of residual vinyl acetate. Panels B, C, D and E show reference spectra of formic acetic anhydride, formyl chloride, acetic acid and carbon monoxide, respectively. Panel F shows the residual product spectrum obtained after subtraction of features due to the identified products (panels B, C, D, E) from the spectrum in panel A.

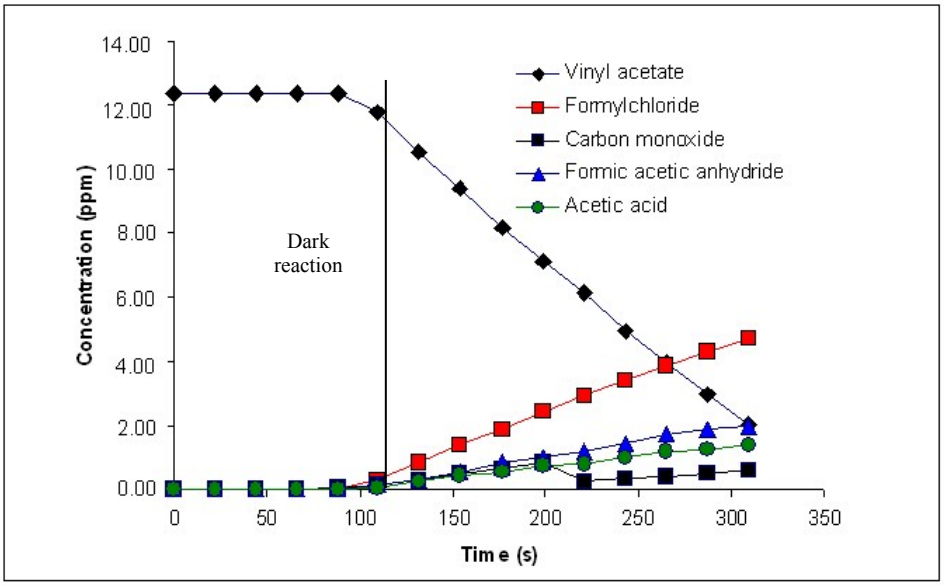

Figure S4: Concentration-time profiles of vinyl acetate (VA) and the reaction products formyl chloride, carbon monoxide acetic acid and formic acetic anhydride obtained from the irradiation of a VA/Cl_2/air reaction mixture.

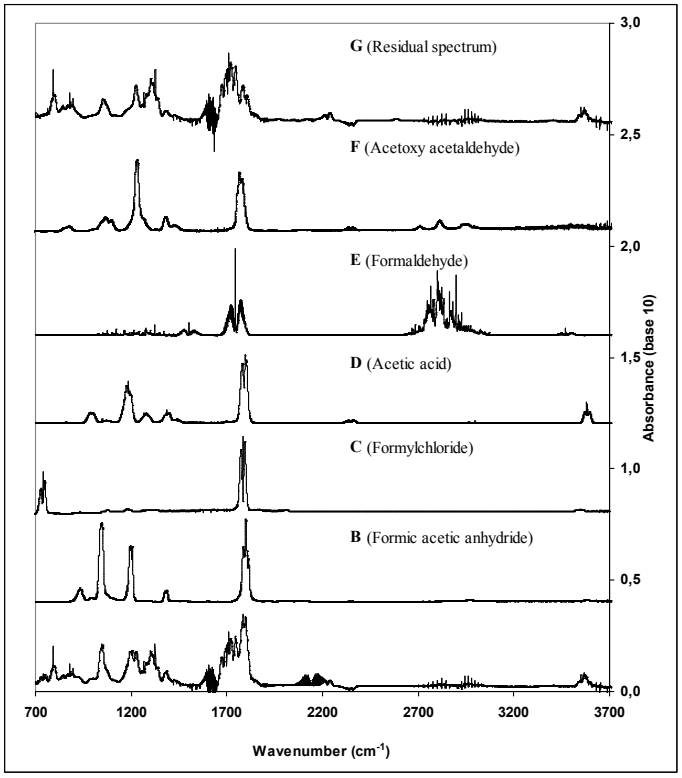

Figure S5: Panel A shows the infrared spectrum of a AA/Cl_2/NO/air reaction mixture after irradiation and subtraction of residual allyl acetate. Panels B, C, D, and F show a reference spectrum of formic acetic anhydride, formyl chloride, acetic acid, formaldehyde and acetoxyacetaldehyde, respectively. Panel G shows the residual product spectrum obtained after subtraction of features due to the identified products (panels B, C, D, E, F) from the spectrum in panel A.

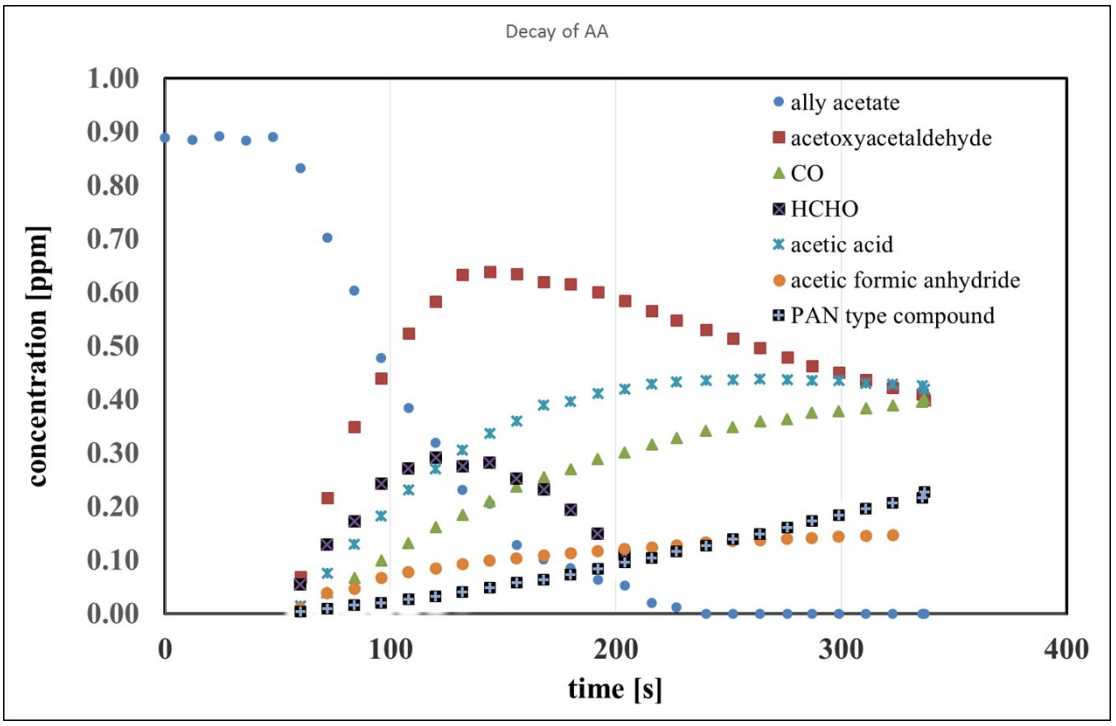

Figure S6: Concentration-time profiles of allyl acetate (AA) and the observed products acetoxyacetaldehyde, acetic acid, formic acetic anhydride, formaldehyde and CO obtained from the irradiation of a AA/Cl_2/NO/air reaction mixture. The observed PAN-type compound ($CH_3C(O)OCH_2C(O)OONO_2$) is plotted as function of the absorbance at 952 cm^{-1} versus time since a calibrated spectrum is not available.

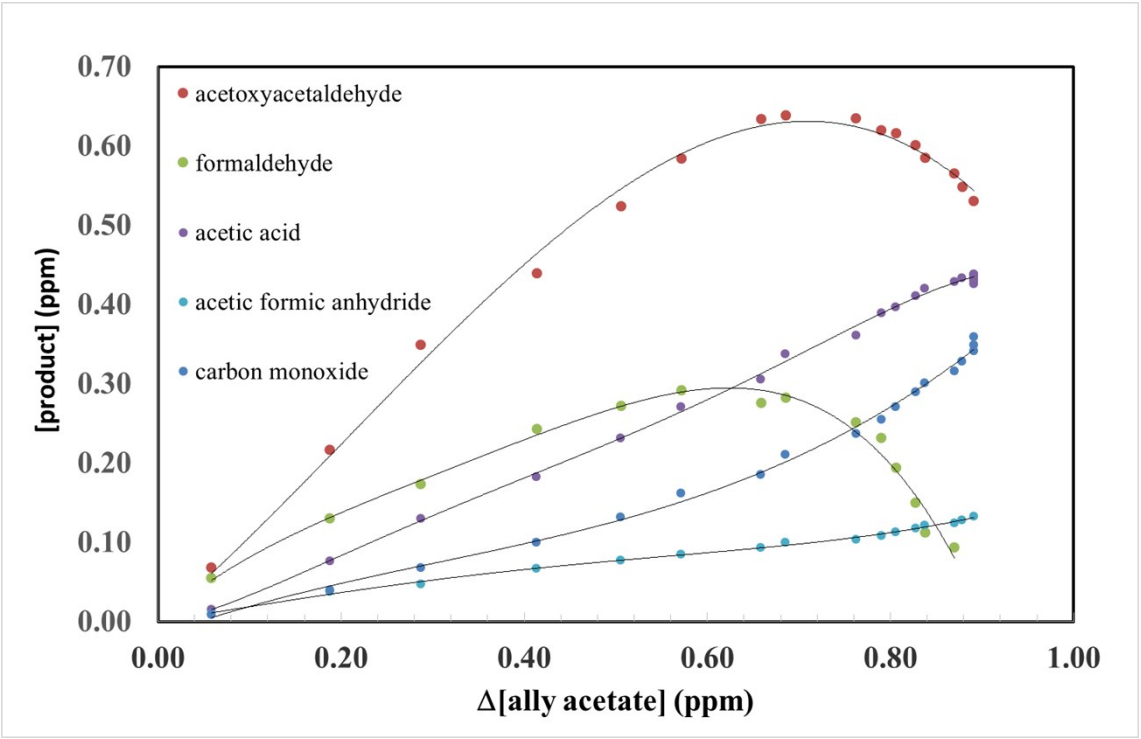

Figure S7: Plot of the concentrations of the products formed in the reaction of Cl with ally acetate (AA) in the presence of NO as a function of the amount of reacted VA.

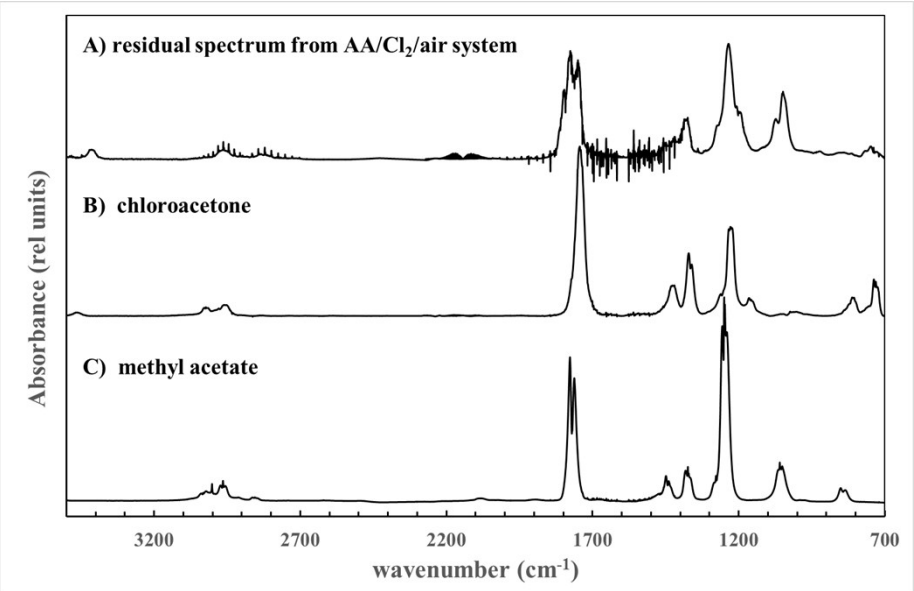

Figure S8: Panel A shows the infrared spectrum of AA/Cl_2/air reaction mixture after irradiation and subtraction of residual allyl acetate and minor contributions from products listed in figure caption S7. Panel B shows a reference spectrum of chloroacetone and panel C a reference spectrum of methyl acetate.

Concentrations, infrared absorption frequencies and chemicals used

The initial concentrations used in the experiments in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) were: 0.52 – 0.81 for VA and 0.39 – 0.84 for AA. The concentration of Cl_2 was typically between 4 to 12 ppm which resulted in Cl atom concentrations of typically 5-10 $\times 10^7$ atoms cm^{-3}. The concentration of NO was typically around 6 ppm.

The following infrared absorption frequencies (in cm^{-1}) were used to monitor the reactants: VA at 1148.6 and AA at 3098.4. Products were monitored at the following absorption frequencies (in cm^{-1}): formaldehyde at 2766; formic acetic anhydride at 1041.4; acetic acid at 1184 and acetoxyacetaldehyde at 1230.

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%), VA (Aldrich**,** 99%), AA (Aldrich**,** 99%), Cl_2 (Messer Griesheim, 2.8) and NO (Messer Griesheim, 99 %).

The absorption cross sections (base 10) for a particular wavelength used in the quantification of the reactants and products were: vinyl acetate: 9×10^{-4} ppm^{-1} m^{-1} (2169 cm^{-1}); allyl acetate: 8×10^{-5} ppm^{-1} m^{-1} (931 cm^{-1}); formic acetic anhydride: 9.6×10^{-19} $molecule^{-1}$ cm^2 (1041 cm^{-1}); acetic acid: 5.65×10^{-4} ppm^{-1} m^{-1} (1184 cm^{-1}); formyl chloride: 66×10^{-20} $molecule^{-1}$ cm^2 (738 cm^{-1}); formaldehyde: 3.1×10^{-4} ppm^{-1} m^{-1} (2766 cm^{-1}); carbon monoxide: 4×10^{-4} ppm^{-1} m^{-1}(2169 cm^{-1}); acetoxyacetaldehyde: 2.14×10^{-20} $molecule^{-1}$ cm^2 (1230 cm^{-1}).