Supplementary Information

for

Tropospheric chemical degradation of vinyl and allyl acetate initiated by Cl atoms under high and low NO\textsubscript{x} conditions

Maria B. Blanco\textsuperscript{a}, Iustinian Bejan\textsuperscript{b,c}, Ian Barnes\textsuperscript{b*}, Peter Wiesen\textsuperscript{b} and Mariano A. Teruel\textsuperscript{a*}

\textsuperscript{a}Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina.

\textsuperscript{b}Physikalische Chemie/FBC, Bergische Universitaet Wuppertal, Wuppertal, Germany.

\textsuperscript{c}“Al. I. Cuza” University of Iasi, Faculty of Inorganic and Analytical Chemistry, Iasi, Romania.

Corresponding authors:
barnes@uni-wuppertal.de (Phone: +49 202 439 2510, Fax: +49 202 439 2505),
mteruel@fcq.unc.edu.ar (Phone: +54 351 4334169/80 int 221, Fax: +54 351 4334188)

Content Summary

Concentration-time profiles in the presence and absence of NO\textsubscript{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\textsubscript{x}, Figure S6.
Yield plots for the products formed from the reaction of Cl with VA in the presence of NO\textsubscript{x} (Figure S2) and for the reaction of Cl with AA in the presence of NO\textsubscript{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\textsubscript{x} (Figure S3), AA in the presence of NO\textsubscript{x} (Figure S5) and AA in the absence of NO\textsubscript{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 acid 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 acid 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/Cl₂/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/Cl₂/air reaction mixture.
Figure S5: Panel A shows the infrared spectrum of a AA/Cl₂/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/Cl₂/NO/air reaction mixture. The observed PAN-type compound (CH₃C(O)OCH₂C(O)OONO₂) 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/Cl₂/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 × 10¹³ 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 Cl₂ was typically between 4 to 12 ppm which resulted in Cl atom concentrations of typically 5-10 × 10⁷ 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%), Cl₂ (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 × 10⁴ ppm⁻¹ m⁻¹ (2169 cm⁻¹); allyl acetate: 8 × 10⁵ ppm⁻¹ m⁻¹ (931 cm⁻¹); formic acetic anhydride: 9.6 × 10⁻¹⁹ molecule⁻¹ cm² (1041 cm⁻¹); acetic acid: 5.65 × 10⁻⁴ ppm⁻¹ m⁻¹ (1184 cm⁻¹); formyl chloride: 66 × 10⁻²⁰ molecule⁻¹ cm² (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 cm² (1230 cm⁻¹).