Interactions of Oxalic Acid and Ice on Cu Surface

Hui Yan and Liang T. Chu
Wadsworth Center, New York State Health Department, and Department of Environmental Health Sciences, State University of New York

Langmuir 2008, 24, 9410-9420
Introduction

- Dicarboxylic acid components are approximately 30-50% of the total organic particulate matter in troposphere.
- Oxalic acid ($C_2H_2O_4$) comprises 37-69% of the total dicarboxylic acids.
- Oxalic acid and its oxalate enhances photochemical hydrogen peroxide production.
- Hydrogen peroxide is responsible for the oxidation of many tropospheric species.
- The hydration or deprotonation of $C_2H_2O_4$ near the ice surface is an important issue to elucidate the nature of the heterogeneous reaction between $C_2H_2O_4$ and bromine on ice surfaces.
Experimental techniques

**RAIRS (reflection absorption infrared spectroscopy)**

**TPD (Temperature Programmed Desorption)**

Various kind of samples

- Adsorption of $\text{H}_2\text{O}$ on $\text{C}_2\text{H}_2\text{O}_4$ covered Cu surfaces ($\text{H}_2\text{O}/\text{C}_2\text{H}_2\text{O}_4/\text{Cu}$)
- Adsorption of $\text{C}_2\text{H}_2\text{O}_4$ on $\text{H}_2\text{O}$ covered Cu surfaces ($\text{C}_2\text{H}_2\text{O}_4/\text{H}_2\text{O}/\text{Cu}$)
- Co-adsorption of $\text{H}_2\text{O}$ and $\text{C}_2\text{H}_2\text{O}_4$ on the Cu surface ($\text{C}_2\text{H}_2\text{O}_4+\text{H}_2\text{O}/\text{Cu}$)
Schematic of the RAIRS-QMS apparatus.
Ice-Film Thickness
The optical interference technique

- A 632.8 nm He-Ne laser beam was incident on the ice-covered Cu surface at 40° from the surface normal.
- The laser beam was reflected at both the vacuum-ice and the ice-Cu interfaces.
- An interference pattern was observed due to the difference in the optical path length of the two reflected beams.
- The thickness $d$ of the ice film at the constructive interference fringes was calculated.
- IR absorbance of the OH bands are used to determine the thickness of the ice film for $d < 140$ nm.
- The integrated RAIR absorbance is proportional to the thickness of thin ice.

$$d = \frac{m \lambda \cos \theta_2}{2n_1 \sin \theta_1 \sin \theta_2 - 2n_2}$$
RAIR spectra of ice films of various thickness depicted at 155 K

The ice-film thickness was 13, 30, 100, 120, 200, and 700 nm, from the lower to the upper solid-line plot

- 2800 to 3700 cm\(^{-1}\) shows OH stretching modes (\(\nu_1\) and \(\nu_3\))
- The band at ~3100 cm\(^{-1}\) is due to reflection of s-radiation and the increased absorption of p-radiation
- The band at ~2250 cm\(^{-1}\) is attributed either to a combination of the bending mode of H\(_2\)O(\(\nu_2\)) with the hindered rotational lattice mode (\(\nu_R\)) or to the third overtone of the hindered rotational lattice mode (3\(\nu_R\))
- Band at ~1640 cm\(^{-1}\) is attributed to the ice bending mode (\(\nu_2\))
- OH dangling band at ~3700 cm\(^{-1}\)(ASW) is not observed suggesting that the ice film on the Cu surface is polycrystalline
Fig 3: TPD spectra for ice and C$_2$H$_2$O$_4$ on the Cu surface

(a) TPD spectrum of 210 nm ice on the Cu surface

(b) TPD spectrum of 5.7 L C$_2$H$_2$O$_4$ on the Cu surface

(c) TPD spectrum for 205 nm ice on the 5.8 L C$_2$H$_2$O$_4$ covered Cu surface

(d) TPD spectrum of 6.2 L C$_2$H$_2$O$_4$ over the 215 nm ice covered Cu surface

(e) TPD spectrum of codeposited 220 nm ice and 5.5 L C$_2$H$_2$O$_4$ on the Cu surface
The desorption temperature ($T_d$) of ice increases with the thickness of the ice film.

Thermal energy is required to break the H-bonding interactions in ice and ice-surface interactions leads to desorption of H$_2$O from the surface.

As thickness increases H$_2$O-H$_2$O attractive interactions (H-bonds) are available, and the total lateral interaction energy is higher hence more thermal energy is required.

H$_2$O desorption temperature for H$_2$O/C$_2$H$_2$O$_4$/Cu is nearly identical to that for H$_2$O/Cu.

The interaction between H$_2$O molecules is weaker than that between C$_2$H$_2$O$_4$ molecules.

C$_2$H$_2$O$_4$ molecules do not desorb along with H$_2$O at the ice $T_d$.

Ice desorption temperature $T_d$ as a function of the film thickness

H$_2$O/Cu
H$_2$O/C$_2$H$_2$O$_4$/Cu
C$_2$H$_2$O$_4$ + H$_2$O/Cu and
C$_2$H$_2$O$_4$/H$_2$O/Cu (see from bottom to top)
Adsorption of C$_2$H$_2$O$_4$ on the Cu surface at 155 K for varying coverages 0.5, 1.4, 2.0, 3.4, 4.0, 5.2, 6.2, 6.6, and 7.4 L from top to bottom

- Band at 1770 cm$^{-1}$ is attributed to the carboxylic stretching mode $\nu_{\text{C=O}}$
- Bands at 1335, 1280, and 1225 cm$^{-1}$ are associated with two coupled modes, the $\delta_{\text{COH}}$ and $\nu_{\text{C-O}}$ modes
- A broad OH stretching band is observed in the range of 2780-3450 cm$^{-1}$ and peaking at approximately 3100 cm$^{-1}$
- Intra- or inter hydrogen bonds among C$_2$H$_2$O$_4$ molecules in the same layer or from the neighboring layers are seen
- At higher coverage the C$_2$H$_2$O$_4$ molecules get H-bonded to each other with different structures as well as surface bonded C$_2$H$_2$O$_4$
- Neither hydrogen oxalate nor oxalate formed on the Cu surface at 155 K
- The adsorbed C$_2$H$_2$O$_4$ is in its molecular state
Desorption of $\text{C}_2\text{H}_2\text{O}_4$ from the Cu Surface

- $\text{C}_2\text{H}_2\text{O}_4$ adsorbs on the Cu surface in two adsorption states when it is deposited on the surface at 155 K (fig 3-b)
- The $T_d$ for sII-$\text{C}_2\text{H}_2\text{O}_4$ (241 K) increases with increasing $\text{C}_2\text{H}_2\text{O}_4$ coverage
- The $T_d$ for sI-$\text{C}_2\text{H}_2\text{O}_4$ is unaffected by the $\text{C}_2\text{H}_2\text{O}_4$ coverage
Fig 6: Adsorption of C₂H₂O₄ on the Cu surface as a function of temperature (155 - 244 K)

- The absorbance of the 1770 cm⁻¹ band increases slightly and the bandwidth narrows
- New bands have appeared at 1320 and 1240 cm⁻¹ on increasing the temperature (h-j)
- sl-C₂H₂O₄ have lower binding energy than ssl-C₂H₂O₄
- When the C₂H₂O₄ layer is heated surfaces are annealed and defects (surface and within the layer) are reduced
Difference spectrum representing subtraction of an IR spectrum of C$_2$H$_2$O$_4$ on the Cu surface at 155K from the corresponding IR spectrum at 225 K

- The peaks at 1795, 1725, 1340, 1275, and 1210 cm$^{-1}$ are associated with the desorbed species up to 225 K ($>T_d$ of sI-C$_2$H$_2$O$_4$)
- The species are either on the top surface layer or at the defect sites and these molecules desorbs first
- The desorbed C$_2$H$_2$O$_4$ (sI-C$_2$H$_2$O$_4$) is associated with weakly bonded C$_2$H$_2$O$_4$ molecules
- The peak at 1795 cm$^{-1}$ is due to surface $\nu_{C=O}$ mode
- The peaks at 1770, 1750, 1320, 1240, and 1190 cm$^{-1}$ correspond to the species existing on the Cu surface at 225 K
- The existing the C$_2$H$_2$O$_4$ (sII-C$_2$H$_2$O$_4$) is associated with strongly H-bonded C$_2$H$_2$O$_4$ analogous to solid C$_2$H$_2$O$_4$

(a) for $\nu_{C=O}$ bands and (b) for $\nu_{C-O}$ and $\delta_{COH}$ bands
(a) 6.2 L C$_2$H$_2$O$_4$/Cu surface
Subtraction of a 200 nm H$_2$O/Cu from 205 nm H$_2$O/5.8 L C$_2$H$_2$O$_4$/Cu

(b') RAIR spectrum for 4 nm H$_2$O/6.3 L C$_2$H$_2$O$_4$/Cu surface this spectrum reveals the spectral features at the interface of H$_2$O and C$_2$H$_2$O$_4$

(C) Subtraction of C$_2$H$_2$O$_4$/H$_2$O/Cu from 215 nm H$_2$O/Cu

(c') Subtraction of C$_2$H$_2$O$_4$/H$_2$O/Cu from 500 nm H$_2$O/Cu

(d) Difference spectrum of C$_2$H$_2$O$_4$+H$_2$O codeposited on the Cu surface
Adsorption of C$_2$H$_2$O$_4$ and H$_2$O on Cu Surface

- It can be seen that the $\nu_{C=O}$ band at 1770 cm$^{-1}$ is shifted to a slightly lower frequency ~1755 cm$^{-1}$ (15 cm$^{-1}$ red-shift).
- The $\nu_{C-O}$ band at 1225 cm$^{-1}$ shifts to a higher frequency, ~1245 cm$^{-1}$ (20 cm$^{-1}$ blue-shift).
- This might be due to the increasing H-bonding interactions between COOH and ice.
- The interaction results in a longer C=O bond length (weaker carbonyl bond C=O) and a shorter C-O bond length (stronger C-O bond).
- The Adsorbed C$_2$H$_2$O$_4$ has two states (sI- and sII-C$_2$H$_2$O$_4$) on the Cu surface.
- It is unknown which of the two states is favored to interact with the ice film.
Fig 9 (a) Subtraction of the RAIR spectrum (a) in Figure 8 to spectrum (b) in Figure 8

(b) Subtraction of a 6.5 L C₂H₂O₄/Cu spectrum from a difference spectrum for 50 nm H₂O/6.5 L C₂H₂O₄/Cu spectrum

- Spectrum (a) reflects the surface and interface vibrational modes of C₂H₂O₄.
- The peak at 1790 cm⁻¹ can be assigned to the ν_{C=O} mode of C₂H₂O₄ on the surface or at the interface.
- The band at 1770 cm⁻¹ could represent the ν_{C=O} vibration either at the interface or in the C₂H₂O₄ layer (many C₂H₂O₄ spectra have this frequency).
- The peak at 1790 cm⁻¹ can be assigned to the ν_{C=O} mode of C₂H₂O₄ on the surface or at the interface.
- The ice-film thickness does not change the frequencies of the bands and the presence of interfacial ν_{C=O} mode is independent of thickness.
Figure 10. RAIR spectra for 680 nm ice deposited on a 6.8 L C$_2$H$_2$O$_4$ covered Cu surface as a function of temperature.

For spectra a-k, the corresponding temperatures are 155, 161, 172, 183, 194, 205, 217, 225, 237, and 283 K.

- Spectra (e-i) is nearly the same as those in spectra (f-j) in Figure 6.
- As the temperature increases, frequency shifts from 1222 to 1240 cm$^{-1}$ and the bandwidth decreases.
- This suggests that the ice adlayer does not dramatically alter the structure of the C$_2$H$_2$O$_4$ layer.
- Nevertheless, the C$_2$H$_2$O$_4$ layer undergoes some structural modification, from less well ordered structure to more highly ordered structure, at the T$_d$ of sI-C$_2$H$_2$O$_4$
- Desorption of ice on the C$_2$H$_2$O$_4$ layer has minimal impact on the structure of the C$_2$H$_2$O$_4$ layer.
Adsorption and desorption of C$_2$H$_2$O$_4$ on Ice-Covered Cu Surfaces at 155 K
(C$_2$H$_2$O$_4$/H$_2$O/Cu)

- IR spectral features for C$_2$H$_2$O$_4$/H$_2$O/Cu are similar to those for H$_2$O/C$_2$H$_2$O$_4$/Cu at 155 K and they are not affected by the ice thickness.
- The C$_2$H$_2$O$_4$ layer and the ice film are little mixed at 155 K as T$_d$ of H$_2$O < T$_d$ of C$_2$H$_2$O$_4$.
- The change of ice T$_d$ indicates that the C$_2$H$_2$O$_4$ adlayer on the H$_2$O/Cu surface alters the ice desorption behavior.
- The changes in desorption profile for both C$_2$H$_2$O$_4$ and ice suggest that the structure of the C$_2$H$_2$O$_4$-ice film altered during the heating process.
- H$_2$O molecules diffuse through the C$_2$H$_2$O$_4$ layer and then desorbs to the gas phase (grain boundaries and defects).
- The interaction between C$_2$H$_2$O$_4$ and ice is weaker than the interaction between C$_2$H$_2$O$_4$ and C$_2$H$_2$O$_4$ (stronger H-bonds, the sublimation enthalpy for C$_2$H$_2$O$_4$ is 98.0 kJ mol$^{-1}$).
The plot indicates that the ice desorption temperature is linearly proportional to \( \text{C}_2\text{H}_2\text{O}_4 \) coverage.
The ice \( T_d \) is limited by \( \text{H}_2\text{O} \) diffusion through the \( \text{C}_2\text{H}_2\text{O}_4 \) layer.
\( \text{H}_2\text{O} \) takes longer time to diffuse through a thicker \( \text{C}_2\text{H}_2\text{O}_4 \) layer.
The diffusion time can be estimated using \( t \approx \frac{d}{2D} \), where \( d \) is the thickness of the \( \text{C}_2\text{H}_2\text{O}_4 \) layer and \( D \) is the diffusion coefficient of \( \text{H}_2\text{O} \) in \( \text{C}_2\text{H}_2\text{O}_4 \).
The temperature is linearly proportion to the time and thus the ice \( T_d \) is linearly proportional to \( \text{C}_2\text{H}_2\text{O}_4 \) coverage.
Desorption of ice in the \( \text{C}_2\text{H}_2\text{O}_4/\text{H}_2\text{O}/\text{Cu} \) system is governed by the diffusion of \( \text{H}_2\text{O} \) through the \( \text{C}_2\text{H}_2\text{O}_4 \) layer.

Figure 11. Desorption temperature \( T_d \) of ice as a function of \( \text{C}_2\text{H}_2\text{O}_4 \) coverage, in the \( \text{C}_2\text{H}_2\text{O}_4/\text{H}_2\text{O}/\text{Cu} \) system.
Bands at 3500, 1266 and a broad band at 1772 cm⁻¹ suggests that H₂O forms a complex \( \{C₂H₂O₄ \cdot (H₂O)_n\} \) with C₂H₂O₄ during the TPD process.

Both the 3500 and the 1266 cm⁻¹ bands disappeared (while the broad 1772 cm⁻¹ band becomes narrower) before temperature reached the \( T_d \) of sI-C₂H₂O₄ (215 K).

This suggests that the complex is metastable and exists at temperatures below the \( T_d \) of sI-C₂H₂O₄.

Formation of complex C₂H₂O₄ \cdot (H₂O)_n depends not only on the stoichiometric ratio of H₂O and C₂H₂O₄ but also on the specific orientations of the H₂O molecules that encounter C₂H₂O₄.

C₂H₂O₄ undergoes structural modifications at the \( T_d \) of sI-C₂H₂O₄, after H₂O is desorbed from the film.
Co-adsorption and desorption of C$_2$H$_2$O$_4$ and H$_2$O on the Cu Surface at 155 K
C$_2$H$_2$O$_4$+H$_2$O/Cu

- C$_2$H$_2$O$_4$ is anticipated to be homogeneously mixed
- Comparing Spectrum (d) in Figure 8 with an IR spectrum of gas-phase C$_2$H$_2$O$_4$ shows that the $\nu_{C=O}$ band is red-shifted from 1820 cm$^{-1}$ in the gas phase to ~1740 cm$^{-1}$ in the C$_2$H$_2$O$_4$-ice mixture
- The magnitude of the red-shift is reasonable, because $\nu_{C=O}$ is 1688 cm$^{-1}$ for oxalic acid dihydrate
- The H$_2$O desorption temperature increases in the following order
- C$_2$H$_2$O$_4$/H$_2$O/Cu > C$_2$H$_2$O$_4$+H$_2$O/Cu > H$_2$O/C$_2$H$_2$O$_4$/Cu ≈ H$_2$O/Cu for comparable ice-film thicknesses and oxalic acid coverages
Figure 13: RAlR spectra of codeposited 6.8 L C$_2$H$_2$O$_4$ and 710 nm ice on the Cu surface. For a-k, the corresponding temperatures are 155, 161, 172, 183, 189, 194, 205, 217, 225, 237, and 242 K.

- A band at 1233 cm$^{-1}$ was observed in spectra (a-d) at T ≤ 183 K.
- At 189 K and 194 K bands at ~3500, 1750, and 1266 cm$^{-1}$ were observed.
- The band at 1750 cm$^{-1}$ is broad and appears to have overlap with lower-wave number bands (1690 cm$^{-1}$).
- A metastable C$_2$H$_2$O$_4$·(H$_2$O)$_n$ complex is formed. However the metastable complex disappears at 205 K as indicated by the loss of the bands at 3500, 1750, and 1266 cm$^{-1}$.

The C$_2$H$_2$O$_4$ layer undergoes a structural modification at ~217 K (bands at 1750, 1310, and 1238 cm$^{-1}$) and C$_2$H$_2$O$_4$ molecules are surrounded by H$_2$O molecules via the van der Waals and H bonding interactions in the codeposited mixture at 155 K.
The analysis of RAIRS and TPD data suggests that interaction between the ice film and C$_2$H$_2$O$_4$ layer occurs primarily at the interface. Neither hydrogen oxalate nor oxalate is formed suggesting that no H$_2$O-induced deprotonation of C$_2$H$_2$O$_4$ takes place in three systems namely H$_2$O/C$_2$H$_2$O$_4$/Cu, C$_2$H$_2$O$_4$/H$_2$O/Cu, and C$_2$H$_2$O$_4$+H$_2$O/Cu over the temperature range 155-283 K. The H$_2$O T$_d$ for CH$_3$COOH/H$_2$O is ~7 K higher than that for H$_2$O/CH$_3$COOH. The interaction between H$_2$O and H$_2$O, via H-bonds, is weaker than that between C$_2$H$_2$O$_4$ and H$_2$O. Ice-C$_2$H$_2$O$_4$ interaction is not sufficiently strong to deprotonate C$_2$H$_2$O$_4$ on/in ice hence ice cannot ionize C$_2$H$_2$O$_4$ into HC$_2$O$_4$ or C$_2$O$_4$~ at 155 K or above. A metastable oxalic acid-ice complex, C$_2$H$_2$O$_4$ · (H$_2$O)$_n$, was observed during the TPD process in the C$_2$H$_2$O$_4$/H$_2$O/Cu and H$_2$O+C$_2$H$_2$O$_4$/Cu systems. C$_2$H$_2$O$_4$ is not in a dissociative state in ice/snow in the polar boundary layer (~240 K) or at upper tropospheric temperatures.