Distillation Kinetics of Solid Mixtures of Hydrogen Peroxide and Water and the Isolation of Pure Hydrogen Peroxide in Ultrahigh Vacuum

M. J. Loeffler,* B. D. Teolis,† and R. A. Baragiola‡

Laboratory for Atomic and Surface Physics, Thornton Hall, University of Virginia, Charlottesville, Virginia 22904-4238

Received: January 15, 2006; In Final Form: February 8, 2006

We present results of the growth of thin films of crystalline H₂O₂ and H₂O₂·2H₂O (dihydrate) in ultrahigh vacuum by distilling an aqueous solution of hydrogen peroxide. We traced the process using infrared reflectance spectroscopy, mass loss on a quartz crystal microbalance, and in a few cases ultraviolet-visible reflectance. We find that the different crystalline phases—water, dihydrate, and hydrogen peroxide—have very different sublimation rates, making distillation efficient to isolate the less volatile component, crystalline H₂O₂.

Introduction

Solid hydrogen peroxide is an interesting material for being one of the simplest molecular solids, and for its role in cold astrophysical environments and in the upper atmosphere of the Earth. The recent discovery of H₂O₂ on the surface of one of Jupiter’s icy moons, Europa, has renewed the interest in this substance and prompted studies inquiring how H₂O₂ can form in that environment, and whether it occurs in pure form or in a solid solution with water.

The properties of solid H₂O₂−H₂O solutions are barely known. Early X-ray diffraction measurements showed that an intermediate compound phase exists in crystalline mixtures, the dihydrate H₂O₂·2H₂O. This compound was also identified in the determination of the equilibrium phase diagram of water−hydrogen peroxide, indicating that when solutions approach equilibrium, there is a competition between the formation of three phases: water, H₂O₂, and the dihydrate. This dihydrate phase was subsequently identified using infrared spectroscopy.

The temperatures at which the dihydrate formed in those experiments (140−200 K) were similar to those on the warmer icy satellites of Jupiter. This prompted us to study the different phases in a vacuum to establish the conditions under which the dihydrate may form in outer space and also to advance understanding of the underlying physicochemical processes.

The scarcity of studies on either pure solid H₂O₂ or aqueous solutions in a vacuum environment is due partly to the difficulty in containing this reactive molecule and partly because high concentrations of H₂O₂ are no longer commercially available. Recently, there has been a report of success in growing H₂O₂ in a vacuum by vapor deposition of gaseous H₂O₂ from urea hydrogen peroxide in a vacuum. We do not follow this method here since we have found that it is inefficient for producing pure solid-phase H₂O₂ by vapor deposition. Instead, we explored the possibility of obtaining pure H₂O₂ and its compound by distillation of an aqueous solution in a vacuum after it is deposited on the substrate, taking advantage of the higher sublimation rate of water than of hydrogen peroxide. The potential of this technique was demonstrated in a previous study of evaporation of a water ice film containing H₂O₂ produced by ion irradiation. Here we present measurements showing the isolation of crystalline H₂O₂ deposits by distillation in ultrahigh vacuum, where we monitor the composition with infrared spectroscopy and the mass loss due to sublimation with a microbalance.

Experimental Setup

All experiments were performed on a radiation-shielded cryostat inside a stainless steel vacuum chamber; the base pressure was (1−4) × 10⁻⁹ Torr and 1−2 orders of magnitude lower inside the shield. H₂O₂−H₂O ice films were grown by vapor deposition using a stainless steel manifold that was passivated by boiling an aqueous solution of 30 wt % H₂O₂ (Alfa Aesar) under oil-free vacuum. This procedure cleansed hydrocarbons on the internal walls of the manifold, thereby reducing production of volatile impurities, such as CO, CO₂, and O₂, generated by reactions of the H₂O₂ with the hydrocarbons. The temperature of the glass ampule containing the solution was held at ~100 °C to increase the pressure of H₂O₂ in the manifold. The films were deposited on the gold mirror electrode of a 6 MHz quartz-crystal microbalance (QCM), which measures the areal mass (mass/unit area).

The deposition temperatures were in the range of 150−173 K, where we determined that the sticking of impurities was undetectable. After growing films in the range of 6−130 µg/cm², we held them at a constant temperature and monitored the mass loss due to sublimation of water and hydrogen peroxide. Since the latter has a lower sublimation rate than water, the concentration of H₂O₂ in the film increases with time; i.e., we distill the film.

The specular infrared reflectance of the films on the gold mirror was measured at an incident angle of 35° with a Thermos-Nicolet Nexus 670 Fourier transform infrared spectrometer at 2 cm⁻¹ resolution, while the specular UV−visible reflectance was measured at an incident angle of 22.5° with an Ocean Optics CCD spectrometer. In both cases, we normalized the spectra by dividing them by the spectrum of the bare gold mirror substrate. In the following we show the normalized spectra in reflectance units R or the optical depth, given by −ln R (Figure 1). To elucidate compositional changes in the films as a result of desorption, we used a differential method: we subtracted

---

† E-mail: bdt4z@virginia.edu.
* To whom correspondence should be addressed. Phone: (434) 924-1059, Fax: (434) 924-1059. E-mail: mjl8r@virginia.edu.
‡ E-mail: raul@virginia.edu.

10.1021/jp060289s CCC: $33.50 © 2006 American Chemical Society Published on Web 03/14/2006
The dihydrate compound \( \text{H}_2\text{O}_2 \) spectrum of the solid solutions have the signatures of water, phases form almost instantaneously. Therefore, the infrared experiments were conducted above 150 K, where the equilibrium is extremely slow in laboratory time scales. However, our are condensed below about 120 K, where molecular diffusion peroxide. Equilibrium phases are not expected when solutions the equilibrium phases are the dihydrate and pure hydrogen concentrations higher than that of the dihydrate (48.6 wt %),

### Results and Discussion

**Crystalline Dihydrate Compound and Crystalline \( \text{H}_2\text{O}_2 \)**

The equilibrium phase diagram of the \( \text{H}_2\text{O}_2-\text{H}_2\text{O} \) system\(^{10}\) for \( \text{H}_2\text{O}_2 \) concentrations below that of the dihydrate shows that the only phases are solid water and dihydrate; no pure hydrogen peroxide precipitates are expected.\(^{10}\) Conversely, at \( \text{H}_2\text{O}_2 \) concentrations higher than that of the dihydrate (48.6 wt %), the equilibrium phases are the dihydrate and pure hydrogen peroxide. Equilibrium phases are not expected when solutions are condensed below about 120 K, where molecular diffusion is extremely slow in laboratory time scales. However, our experiments were conducted above 150 K, where the equilibrium phases form almost instantaneously. Therefore, the infrared spectrum of the solid solutions have the signatures of water, the dihydrate compound \( \text{H}_2\text{O}_2-2\text{H}_2\text{O} \), and pure \( \text{H}_2\text{O}_2 \) (Figure 1 and Tables 1 and 2), depending on the \( \text{H}_2\text{O}_2 \) concentration. It is important to note that since the experiments are done in a vacuum, the continuous evaporation implies that we are moving gradually in the phase diagram toward regions of higher \( \text{H}_2\text{O}_2 \) concentration.

We performed distillation of \( \text{H}_2\text{O}_2-\text{H}_2\text{O} \) mixtures at two temperatures: 154.4 and 166 K. After the film was deposited at 154.4 K, the optical depth spectra (Figures 2 and 3, compared to Figure 1) show that both water and hydrogen peroxide leave the film, with water being lost preferentially. In addition, we obtained mass loss rates due to sublimation by taking the time derivative of the areal mass given by the QCM. Figure 4 shows that the sublimation rate decreases with time, while significant changes occur in the differential infrared signature of the desorbing species (Figure 5). By the time there is 7.36 changes occur in the differential infrared signature of the sublimation rate (at 6700 to 8100 s in Figure 4). At the same time, the bending bands of \( \text{H}_2\text{O}_2 \) in the infrared spectra change only slightly due to the loss of water.

### Table 1: \( \text{H}_2\text{O}_2-2\text{H}_2\text{O} \) Dihydrate Absorption Bands (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>peak position</th>
<th>assignment</th>
<th>peak position</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1391.4(8), m</td>
<td>( \nu_6 )</td>
<td>2852(1), s</td>
<td></td>
</tr>
<tr>
<td>1459.6(10), w</td>
<td>( \nu_2 )</td>
<td>2997(2), vw</td>
<td></td>
</tr>
<tr>
<td>1648(8) broad, w</td>
<td>( \nu_2 ) (( \text{H}_2\text{O} ))</td>
<td>3165(1), vs</td>
<td>( \nu_1 )</td>
</tr>
<tr>
<td>2212(6) broad, w</td>
<td>( \nu_2 + \nu_6 ) (( \text{H}_2\text{O} ))</td>
<td>3427(1), vs</td>
<td></td>
</tr>
<tr>
<td>2753(2), vw</td>
<td></td>
<td>5053(20) broad</td>
<td></td>
</tr>
</tbody>
</table>

\( \nu_6 \), \( \nu_2 \), and \( \nu_1 \) are characteristic of crystalline \( \text{H}_2\text{O}_2 \). We note that the transition from water plus dihydrate to only dihydrate seen in the infrared spectrum between 9.6 and 7.3 \( \text{K} \) is accompanied by a change in the sublimation rate (at \( \sim6700 \) to \( 8100 \) s in Figure 4). At the same time, the bending bands of \( \text{H}_2\text{O}_2 \) in the infrared spectra change only slightly due to the loss of water.

### Table 2: Crystalline \( \text{H}_2\text{O}_2 \) Absorption Bands (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>peak position</th>
<th>assignment</th>
<th>peak position</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1332.5(10), m</td>
<td>( 2\nu_3 )</td>
<td>3182.2(4), vs</td>
<td>( \nu_5 )</td>
</tr>
<tr>
<td>1388.4(10), s</td>
<td>( \nu_4 )</td>
<td>3287.1(6), vs</td>
<td>( \nu_1 )</td>
</tr>
<tr>
<td>1416.5(10), s</td>
<td>( \nu_5 )</td>
<td>3316(4), sh</td>
<td></td>
</tr>
<tr>
<td>2264(3), vw</td>
<td></td>
<td>3392(3)</td>
<td></td>
</tr>
<tr>
<td>2337.5(5), m</td>
<td></td>
<td>3957(10), sh</td>
<td></td>
</tr>
<tr>
<td>2362.0(5), m</td>
<td></td>
<td>4075(7) broad</td>
<td></td>
</tr>
<tr>
<td>2395(1), vw</td>
<td></td>
<td>4566(10), sh</td>
<td></td>
</tr>
<tr>
<td>2460(5) broad, vw</td>
<td></td>
<td>4628(3), w</td>
<td></td>
</tr>
<tr>
<td>2730(3), sh</td>
<td></td>
<td>4664(2), w</td>
<td></td>
</tr>
<tr>
<td>2754 (2), m</td>
<td></td>
<td>4725 (10), (sh)</td>
<td></td>
</tr>
<tr>
<td>2805(3), m</td>
<td></td>
<td>6220 plateau, vw</td>
<td></td>
</tr>
<tr>
<td>2843(3), m</td>
<td></td>
<td>6425(20) broad</td>
<td></td>
</tr>
</tbody>
</table>

\( \nu_5 \) \( \nu_1 \) \( \nu_3 \) assignments are from Giguere and Harvey.\(^{11}\) Sh, shoulder. Qualitative absorption strengths are indicated by the following: s, strong; m, medium; w, weak; vw, very weak. The numbers in parentheses are uncertainties in the last significant figure.
The infrared spectra showed that the film eventually became pure H$_2$O$_2$, with negligible sublimation rate (Figure 4, top). Now we analyze the case of films deposited at a higher temperature: 166 K. In this case, the as-deposited film is similar in thickness to the one grown at 154.4 K but it has a higher H$_2$O$_2$ concentration (and amount) because of a decreased sticking coefficient of water. At 166 K, the distillation proceeded as at 154.4 K but with a reduced time scale due to higher sublimation rates. We note that the sublimation rate during the experiments dropped by nearly 2 orders of magnitude when going from the sublimation of water to that of hydrogen peroxide (Figure 4, top). In Figures 6 and 7, we show the evolution of optical depth spectra (beginning at 15.3 mg/cm$^2$ at 1500 s in Figure 4) after crystalline water has already desorbed and only the dihydrate and pure H$_2$O$_2$ remain on the substrate. Late in the distillation, the stretching vibrations $\nu_1$ and $\nu_3$ (Figure 6), bending vibrations $\nu_2$ and $\nu_6$ (Figure 7), and bending overtone regions (Figure 8), characteristic of pure H$_2$O$_2$, are visible in the infrared spectra.

The crystalline H$_2$O$_2$ films obtained at long times are very stable: after more than 12 h at 166 K, there were no observable changes in the infrared spectra besides a slight decrease of the absorption due to sublimation of the film. After distillation the purity of these films is 98% crystalline H$_2$O$_2$. This value is based on experiments where we added known amounts of water to H$_2$O$_2$ while measuring the absorption band of water at 1650 cm$^{-1}$. The conclusion is also consistent with published spectra for films of approximately the same thickness.

**Effect of Sublimation on Optical Reflectance.** We measured the UV–visible (300–700 nm) reflectance during film deposition at 100 and at 167 K. At 100 K we observed well-pronounced oscillations in reflectance between 300 and 500 nm caused by interference between reflections from the substrate and the film surfaces. In contrast, when the films were grown at 167 K, there was no indication of oscillations because the specular reflectance was attenuated by light scattering off the film. This effect was most prominent in the visible but also apparent in the infrared (Figure 9). This wavelength dependence (reddening) indicates Rayleigh scattering from small imperfections; their nature is not clear at present, but they may be boundaries between grains or precipitates, surface roughness, and microcracks, etc. These reflectance measurements were consistent with visual inspection of the film, which looked hazy.
and nonuniform. Also in the specular direction the film appeared red to the eye.

After we stopped deposition at 167 K, we monitored the temporal changes in the sublimation rate and in the optical reflectance of the sample. Sublimation proceeded similarly to that shown in Figure 4. After 9 1/2 h, when the infrared spectrum showed the signature of only hydrogen peroxide, the specular reflectance in the visible and lower infrared wavelengths increased substantially (Figure 9), indicating a decrease in scattering. This effect may be due to homogenization of the film by loss of the dihydrate phase or by the growth of the $\text{H}_2\text{O}_2$ precipitates. Visual inspection also supports the increase in homogeneity; we found that after the dihydrate sublimes the appearance of the reflected light to the eye changed from red to white and specular reflection became prominent, even though the film still appeared somewhat hazy in an off-specular position.
Conclusions

Here we have demonstrated a method for the growth, in ultrahigh vacuum, of films of controlled composition of H_2O_2 and H_2O_2·2H_2O by distillation, avoiding the risk of decomposition or contamination by reactions with system walls. Above ~150 K, different phases precipitate quickly, as expected from the equilibrium phase diagram. Sublimation results in the loss of material according to the volatility of the species: first water, then the dihydrate, and finally, H_2O_2, the least volatile. The use of the microbalance allows us to quantify the distillation process. At the higher temperatures tried in this study, 166–167 K, the decreased sticking of water molecules led to films with higher H_2O_2 concentrations. Distillation resulted in crystalline H_2O_2 with negligible amounts of impurities detectable by infrared spectroscopy. This method of preparation should be useful for further studies of pure hydrogen peroxide and could be extended to other reactive condensed gases, which are not easily handled in their pure form. Finally, our results show that the dihydrate compound may form at temperatures that exist in the mesosphere of the Earth and in warmer regions of the outer solar system.

Acknowledgment. This research was supported by NASA Planetary Atmospheres and NSF Astronomy programs. M.J.L. thanks the Virginia Space Grant Consortium for a scholarship.

References and Notes