IR Detection of $\text{H}_2\text{O}_2$ at 80 K in Ion-Irradiated Laboratory Ices Relevant to Europa

M. H. Moore

Code 691, Astrochemistry Branch, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771
E-mail: ummhm@lepvax.gsfc.nasa.gov

and

R. L. Hudson

Department of Chemistry, Eckerd College, St. Petersburg, Florida 33733

Received June 7, 1999; revised November 17, 1999

We present the first in situ laboratory detection of $\text{H}_2\text{O}_2$ in $\text{H}^+$-irradiated ices at temperatures relevant to the icy Galilean satellites. These experiments were motivated by the recent Galileo NIMS detection on Europa of a 3.5-$\mu$m band identified with $\text{H}_2\text{O}_2$ (R. W. Carlson et al. 1999, Science 283, 2062-2064). In our laboratory experiments, the IR signature of $\text{H}_2\text{O}_2$ was easily observed after irradiation of pure $\text{H}_2\text{O}$ at 16 K, but it was not seen after irradiation at 80 K. Radiolysis of mixtures of $\text{H}_2\text{O}$ with $\text{O}_2$ or $\text{CO}_2$ at 80 K did produce $\text{H}_2\text{O}_2$. These results show that ices more complex than pure $\text{H}_2\text{O}$ are involved in the radiolysis pathway to form $\text{H}_2\text{O}_2$ on Europa. We also report the intrinsic band strength and radiation yield of $\text{H}_2\text{O}_2$ in ice mixtures, along with possible formation and destruction mechanisms. Sufficient concentrations of $\text{H}_2\text{O}_2$ can be formed in $\text{H}_2\text{O}$ ices containing $\text{O}_2$ to explain the NIMS observation.

Key Words: radiation chemistry; ices; Europa; infrared observations; satellites of Jupiter.

INTRODUCTION

Hydrogen peroxide has been identified on Europa based on a 3.50-$\mu$m absorption feature in Galileo NIMS spectra, along with corroborating evidence from profiles at shorter wavelengths in Galileo UVS spectra (Carlson et al. 1999). The position and width of the IR feature were matched with a laboratory reflectance spectrum of $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ ice; the intensity of the NIMS feature suggested an $\text{H}_2\text{O}_2$ concentration of 0.13% by number relative to $\text{H}_2\text{O}$. Europa has a constant flux of energetic ions bombarding its surface, therefore $\text{H}_2\text{O}_2$ is thought to be a radiation product. Based on the reported radiation yield for $\text{H}_2\text{O}_2$ in $\text{H}_2\text{O}$ ice, Carlson et al. (1999) concluded that the surface abundance of $\text{H}_2\text{O}_2$ on Europa, after factoring in production and loss rates thought to be relevant, would be 0.013 to 0.3% relative to $\text{H}_2\text{O}$, a number consistent with the observations.

Table I summarizes the known condensed-phase molecules on Europa, Ganymede, and Callisto. These satellites of Jupiter have $\text{H}_2\text{O}$ ice on their surfaces. Condensed-phase molecular oxygen has been detected on Ganymede along with $\text{O}_3$; on Europa a tenuous oxygen atmosphere has been observed (Hall et al. 1998). All of these icy satellites exist in the radiation environment of Jupiter, and the intensities and energies of particles ($\text{H}^+$, $\text{O}^+$, $\text{S}^+$, and $\text{e}^-$) bombarding their surfaces varies with, e.g., the distance of the satellite from Jupiter, and the satellite’s intrinsic magnetic field and atmospheric density. The estimated value of the incident energy flux (Cooper et al. 2000) is included in Table I for each satellite. Although Europa receives the highest flux of energetic particles, the other satellites receive enough radiation that the formation of products like $\text{H}_2\text{O}_2$ seems likely.

The influence of ionizing radiation on frozen water has been studied for many years with most early work focusing on the identities and yields of stable products, namely $\text{H}_2$, $\text{O}_2$, and $\text{H}_2\text{O}_2$. In a typical experiment, an ice was irradiated and subsequently melted for analysis. Since transient, highly reactive species like trapped electrons, OH, H, and HO$_2^-$, cannot be detected this way, they have been studied at low temperatures with in situ methods such as UV-visible spectroscopy or electron spin resonance spectroscopy. Pulse radiolysis also has been employed for detection of transients in irradiated ice.

Traditionally the yield of a radiation product has been denoted by a $G$ value, defined as the number of molecules of a certain type formed per 100 eV of energy absorbed. Numerous workers have studied $\text{H}_2\text{O}_2$ production in ice and reported on how $G(\text{H}_2\text{O}_2)$ and the final $\text{H}_2\text{O}_2$ abundance are influenced by temperature, the initial composition of the ice, and the type of radiation used. For example, Ghormley and Stewart (1956) measured $\text{H}_2\text{O}_2$ production in ice $\gamma$-irradiated at several temperatures, and found that the final abundance of $\text{H}_2\text{O}_2$ was lowest at their highest irradiation temperatures. However, they also found
that at the higher irradiation temperatures the amount of H$_2$O$_2$ formed could be increased by adding O$_2$ to the ice before freezing and irradiating. In all cases the irradiated ices had to be melted for H$_2$O$_2$ analysis; no in situ H$_2$O$_2$ determinations were possible.

Although γ- and X-ray experiments provide insight into the radiation chemistry of ice, ion irradiations are more relevant to icy satellites. Unfortunately, in situ measurements of $G$(H$_2$O$_2$) are also lacking for ion irradiations. The Galileo NIMS data was interpreted (Carlson et al. 1999) with $G$(H$_2$O$_2$) = 0.4 for α irradiation of ice; however, the source of this value is surprisingly elusive. We have traced this $G$(H$_2$O$_2$) to Lefort (1955), a paper which gives few analytical details of the H$_2$O$_2$ analysis. However, earlier papers (Bonet-Maury and Lefort 1948, Bonet-Maury and Frilley 1944, Bonet-Maury 1941, 1944) make it clear that the irradiated ices were melted prior to measurement of $G$(H$_2$O$_2$) near room temperature with a colorimetric method.

In this paper we present laboratory results for proton-irradiated ices, along with in situ measurements of H$_2$O$_2$ production. By studying these ices in the solid state, we are able to avoid the uncertainties introduced by melting samples for H$_2$O$_2$ analysis. The temperatures chosen for our irradiations and H$_2$O$_2$ analyses were 16 and 80 K, the latter being more relevant for jovian satellites. Although H$_2$O$_2$ was easily observed after irradiation of pure H$_2$O ice at 16 K, contrary to our expectations it was not seen after irradiation at 80 K. If, however, the 80 K H$_2$O ice contained either O$_2$ or CO$_2$, then H$_2$O$_2$ was detected after irradiation. Overall, the band position and width of the H$_2$O$_2$ feature showed some variation with composition, concentration, and temperature. We also have measured the intrinsic IR band strength, the A value, of the H$_2$O$_2$ band near 3.5 μm, the same band used to identify H$_2$O$_2$ in the NIMS data. The H$_2$O$_2$ band strength and our IR spectra after irradiation have been combined to give H$_2$O$_2$ yields for different ice mixtures.

### EXPERIMENTAL

Ice films a few microns in thickness were formed in two different ways on an aluminum mirror attached to the tail section of a closed-cycle cryostat. First, for each irradiation experiment an ice film was formed by gas-phase condensation at 16 K, and the resulting ice thickness was determined by measuring interference fringes during deposition. Second, ices of H$_2$O + H$_2$O$_2$ were made by using a syringe to inject a solution through a vacuum septum onto the precooled mirror (~16 K). In both cases, the ice temperature could be maintained between ~16 and 300 K. The results reported in this paper do not depend on the precise value of the minimum temperature.

Infrared absorption spectra of all ices were measured by passing an IR beam through the ice film, reflecting it from the ice–aluminum interface, and again passing it through the ice. However, analysis of spectra to calculate column density was based on the physical thickness of the ice, not the IR thickness. The resolution of the spectrometer for these experiments was 4 cm$^{-1}$. Reported spectral positions are accurate to ±0.5 cm$^{-1}$.

Protons (0.8 MeV) from a Van de Graaff accelerator were used to irradiate ices at 16 and 80 K. A nickel beam foil separated the vacuum of the accelerator from the clean vacuum of the cryostat area. Details of this experimental setup are already in print (Moore et al. 1996, Hudson and Moore 1995, and references therein).

Quantitative analysis of IR spectra of irradiated ices involved two steps. First, $A$(H$_2$O$_2$) for the 3.5-μm band had to be measured. The injection technique was used to form different thicknesses of H$_2$O + H$_2$O$_2$ ice at ~16 K. The area of the H$_2$O$_2$ (3.5 μm) band was plotted against the area of the H$_2$O band at 753 cm$^{-1}$ (13.3 μm) for each ice thickness. The slope of a line connecting these data is proportional to $A$(H$_2$O$_2$)/$A$(H$_2$O), the value of $A$(H$_2$O) being known at ~16 K from Hudgins et al. (1993). Our data gave $A$(H$_2$O$_2$) = 2.7 × 10$^{-17}$ cm molecule$^{-1}$ at ~16 K. Next, the H$_2$O$_2$ band in each irradiated ice was integrated for every proton dose. Dividing the integrated band’s areas by $A$(H$_2$O$_2$) gave the column density of H$_2$O$_2$ in each ice as a function of radiation dose. To compare our results with estimates of the %H$_2$O$_2$ on Europa, column densities of H$_2$O$_2$ were converted to %H$_2$O$_2$ by number relative to H$_2$O.

The sources and purities of the reagents used in these experiments are as follows: triply distilled H$_2$O with a resistance greater than 10$^{7}$ ohm cm; H$_2$O$_2$ (J. T. Baker), 30%; H$_2$O$_2$, standard pharmaceutical reagent, 3%; O$_2$ (Matheson), 99.6%; 18O$_2$ (Alfa), 99% 18O; CO$_2$ (Matheson), 99.995%; C$^{18}$O$_2$ (Isomet), 95% 18O; N$_2$O (Airco), 99%.

### TABLE I

<table>
<thead>
<tr>
<th>Icy Galilean Satellites</th>
<th>Condensed phase molecules identified</th>
<th>Temperature range</th>
<th>Total average energy flux, $E &gt; 20$ keV$^a$ (eV cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europa</td>
<td>H$_2$O, CO$_2$, SO$_2$, H$_2$O$_2$</td>
<td>85–128 K</td>
<td>78 × 10$^{12}$</td>
</tr>
<tr>
<td>Ganymede</td>
<td>H$_2$O, CO$_2$, SO$_2$, O$_2$</td>
<td>85–152 K</td>
<td>5.4 × 10$^{12}$ poles</td>
</tr>
<tr>
<td>Callisto</td>
<td>H$_2$O, CO$_2$, SO$_2$, O$_2$, O$_3$</td>
<td>80–150 K</td>
<td>0.2 × 10$^{12}$ equator</td>
</tr>
</tbody>
</table>

$^a$ Cooper et al. (2000), lower limit of energetic ions and electron flux based on EPD experiment on Galileo Orbiter.

$^b$ Smythe et al. (1998).

$^c$ Lane et al. (1981), Noll et al. (1995).

$^d$ Carlson et al. (1999).

$^e$ Orton et al. (1996).

$^f$ Hanel et al. (1979).

$^g$ Carlson et al. (1996), McCord et al. (1997), McCord et al. (1998).


$^i$ Spencer et al. (1995).

$^j$ Noll et al. (1996).

$^k$ Noll et al. (1997).

$^l$ Associated with impact area.
RESULTS

(a) IR Spectrum of H$_2$O + H$_2$O$_2$

Figure 1 shows the IR spectrum of H$_2$O + H$_2$O$_2$ at 16 K from 3.2–4.0 μm. The H$_2$O$_2$ concentration was determined by KMnO$_4$ titration, before injection, to be 2.66% by mass or 1.4% by number relative to H$_2$O. The band at 2855 cm$^{-1}$ (3.503 μm) in Fig. 1, with a full width at half maximum (FWHM) of 74 cm$^{-1}$ (0.09 μm), was identified with the $v_2 + v_b$ combination mode (also possibly $2v_b$ and $2v_2$) of H$_2$O$_2$ (Lannon et al. 1971, Pettersson et al. 1997). The underlying, sloping continuum on which the H$_2$O$_2$ feature sits in Fig. 1 is part of the 3260 cm$^{-1}$ (3.07 μm) water band. This same H$_2$O$_2$ absorption was measured at 80 K by diffuse reflection (Carlson et al. 1999), after cooling a liquid H$_2$O$_2$ solution from room temperature, and found to be at 2854 cm$^{-1}$ (3.504 μm) with a FWHM of 49 cm$^{-1}$ (0.06 μm). We warmed a 1.4% H$_2$O$_2$ ice from 16 to 160 K and found that the band position changed from 2855 cm$^{-1}$ (3.503 μm) to 2845 cm$^{-1}$ (3.515 μm) and the FWHM decreased as the sample became crystalline. Similar behavior was observed on warming a more concentrated sample, 14% H$_2$O$_2$, to 160 K.

(b) Irradiated Pure H$_2$O

A 3-μm-thick film of H$_2$O was irradiated at ~16 K to a total dose of 17 eV molecule$^{-1}$. After irradiation H$_2$O$_2$ was detected on the wing of the H$_2$O band, with a peak position at 2856 cm$^{-1}$ (3.501 μm) and a FWHM of 49 cm$^{-1}$ (0.06 μm). The position and width of this H$_2$O$_2$ band were essentially unchanged from ~16 to 120 K. The experiment was then repeated at 80 K, but to our surprise no H$_2$O$_2$ was detected after irradiation. This result led us to examine the radiolysis of icy mixtures relevant to Europa which might form H$_2$O$_2$.

(c) Irradiated H$_2$O + O$_2$

To investigate the influence of the addition of O$_2$ to H$_2$O on the formation of H$_2$O$_2$, we condensed a gaseous mixture of H$_2$O + O$_2$ (8:1) at ~16 K. The ice was slowly warmed to 80 K and then irradiated. This 8:1 mixture gave a very clear H$_2$O$_2$ feature at 2841 cm$^{-1}$ (3.520 μm) with a FWHM of 121 cm$^{-1}$ (0.15 μm). Figure 2 shows the change in the abundance of H$_2$O$_2$ in this irradiated ice as a function of deposited energy.

Although pure O$_2$ vaporizes in our 10$^{-7}$ torr vacuum near 30 K, we expected that some O$_2$ would be trapped in the bulk ice (Ghormley 1967) during warming to 80 K. One indication of the presence of trapped O$_2$ was the IR detection of the $v_3$ mode of O$_3$ at 1034 cm$^{-1}$ (Brewer and Wang 1972) after irradiating the 80 K H$_2$O + O$_2$ ice. We estimate that ~60% of the O$_2$ is retained in the H$_2$O ice during warming, which results in an H$_2$O + O$_2$ (~100:8) at 80 K. This result is based on a comparison of the areas of the O$_3$ band formed for similar radiation doses on H$_2$O + O$_2$ (8:1) ices at 18 K and that same original ice composition warmed and irradiated at 80 K. The estimate assumes that the yield of O$_2$ → O$_3$ is the same at both temperatures.

(d) Irradiated O$_2$ on Top of H$_2$O (O$_2$/H$_2$O)

In another experiment, H$_2$O$_2$ formed in H$_2$O ice irradiated at 80 K when some O$_2$ was present at or near the surface of the ice. This condition was created by first forming a few-micrometers-thick layer of H$_2$O ice at ~16 K and then adding an equal thickness of O$_2$ ice on top of it (notation for this layered experiment is: O$_2$/H$_2$O). This layered ice was slowly warmed to 80 K before irradiation. Although most of the O$_2$ vaporized during warming, some fraction was bound to the water surface or was trapped in the top portion of the porous amorphous water ice (Ghormley 1967). After irradiation, H$_2$O$_2$ was detected in the infrared spectrum at 2851 cm$^{-1}$ (3.508 μm) with a FWHM of
83 cm$^{-1}$ (0.10 μm). A factor of 2–3 less H$_2$O$_2$ was formed in this experiment compared with the experiment where O$_2$ was more intimately mixed and trapped in the bulk ice. Results from this O$_2$/H$_2$O experiment are also plotted in Figure 2. The smaller amount of trapped O$_2$ probably explains why O$_3$ was not detected in this experiment. Without the formation of detectable O$_3$ we were unable to estimate the amount of O$_2$ trapped on the surface at 80 K.

(e) H$_2$O + CO$_2$

Since CO$_2$ has also been identified on the surface of Europa (Table I), we studied irradiated H$_2$O + CO$_2$ (8:1) ice to examine other possible formation pathways for H$_2$O$_2$. Irradiated H$_2$O containing CO$_2$ formed H$_2$O$_2$ with a broad band at 2851 cm$^{-1}$ (3.508 μm) and a FWHM of 101 cm$^{-1}$ (0.12 μm). Figure 2 shows the change in percentage abundance of H$_2$O$_2$ in the irradiated ice at 80 K as a function of radiation dose.

(f) Other Ice Mixtures

A few supporting experiments were done at ~16 and 80 K with isotopically labeled molecules. A 10:1 mixture of H$_2$O + C$^{18}$O$_2$ was irradiated, and H$_2$O$_2$ was seen at the same position as in the H$_2$O + C$^{16}$O$_2$ mixture. An 8:1 H$_2$O + $^{18}$O$_2$ mixture was irradiated, and the peak position of H$_2$O$_2$ occurred 10 wave-numbers less than in the H$_2$O + $^{16}$O$_2$ experiment.

Many other experiments were performed to determine if H$_2$O$_2$ formation was common in irradiated ice mixtures. Ices made of H$_2$O and other molecules, containing carbon, hydrogen, nitrogen, and oxygen, did not produce H$_2$O$_2$ during irradiation with one exception. When a 10:1 mixture of H$_2$O + N$_2$O (nitrous oxide) was irradiated, at either 16 or 80 K, the 3.50-μm band of H$_2$O$_2$ band was easily observed. The significance of this experiment will be discussed below. We hope to extend our work to sulfur-containing molecules in the near future.

DISCUSSION

(a) Comparison of Laboratory Spectra with the Europa Spectrum

In our experiments, the 3.5-μm H$_2$O$_2$ band’s position and width were influenced by several factors. First, the position of the band changed with ice composition. In O$_2$/H$_2$O and H$_2$O + CO$_2$ irradiated ices at 80 K the peak positions were within the limits of the observed H$_2$O$_2$ feature on Europa, 3.50 ± 0.015 μm. However, the location of the H$_2$O$_2$ band in our H$_2$O + O$_2$ experiment was outside the limits of the Europa observation by +0.005 μm. Second, we found that the position of H$_2$O$_2$ in H$_2$O$_2$ mixtures depended on the H$_2$O$_2$ concentration. In a 1.4% H$_2$O$_2$ solution frozen at ~16 K the peak was at 2855 cm$^{-1}$ (3.503 μm), but at 2843 cm$^{-1}$ (3.517 μm) for a similarly frozen 14% solution. The FWHM of the 3.5-μm band in these icy mixtures varied from 74 to 96 cm$^{-1}$ (0.09–0.12 μm, respectively). The width of the H$_2$O$_2$ band in the Europa observation, and the H$_2$O$_2$ 80 K reference spectrum measured by Carlson et al. (1999) in diffuse reflection, was ~49 cm$^{-1}$ (0.06 μm). Finally, we observed that the FWHM of the H$_2$O$_2$ band in both the 1.4% and the 14% H$_2$O$_2$ ice decreases ~40% from 18 K (a temperature where the phase of H$_2$O ice is amorphous) to 160 K (a temperature where the phase of H$_2$O ice is crystalline). Table II summarizes the peak position and FWHM of the 3.5-μm H$_2$O$_2$ band observed for different conditions.

Carlson et al. (1999) concluded that their laboratory measurements indicated a surface concentration of H$_2$O$_2$ on Europa near 0.13%, by number relative to water ice. This concentration is at the limit of detectability for transmission IR spectra of synthesized H$_2$O$_2$ in laboratory ices, which we estimated to be at the 0.1–0.2% level. Variations in the peak position and width depend on the composition and H$_2$O$_2$ concentration of the ice along with other factors such as grain size, porosity, and thermal history. Detectability of weak features may also be affected by the difference between diffuse reflection measurements of bulk ice compared to absorption in a thin film. The identification and suggested concentration of H$_2$O$_2$ on Europa given by Carlson et al. (1999) is consistent with our laboratory experiments. It is the nature of the ices that leads to the H$_2$O$_2$ formation that is more complex than previously thought.

(b) Yield of H$_2$O$_2$

We have calculated in situ yields of H$_2$O$_2$ for the experiments done at 80 K. These yields are more relevant for icy satellites than those from previous studies on H$_2$O$_2$, where $G$(H$_2$O$_2$) was measured after the irradiated ice had been melted. Our $G$ values are calculated during the early part of experiments when the production of H$_2$O$_2$ increases linearly with dose. The slopes for the curves in Fig. 2 give $G$(H$_2$O$_2$) for each ice studied. We used all of the data points for H$_2$O + O$_2$ and O$_2$/H$_2$O and the first data point for H$_2$O + CO$_2$ ice to determine the slopes. $G$ determined at higher doses in these experiments are less useful because product saturation occurs. The average $G$(H$_2$O$_2$) for the H$_2$O + O$_2$ experiment was 0.41, for O$_2$/H$_2$O it was 0.16, and for H$_2$O + CO$_2$ it was 0.10. For comparison, $G$(H$_2$O$_2$) = 0.1 in pure H$_2$O at ~16 K.

From the range of our $G$(H$_2$O$_2$s) 0.1 to 0.4, the estimated steady-state percentage abundance of H$_2$O$_2$ on Europa is 0.07–0.28% assuming a lifetime of 100 days and an energy flux of 50 × 10$^{12}$ eV cm$^{-2}$ s$^{-1}$ as discussed by Carlson et al. (1999). The $G$(H$_2$O$_2$) = 0.4 they used, which was based on analyses of ices melted after irradiation, was the largest $G$(H$_2$O$_2$) we measured in situ for our H$_2$O + O$_2$ irradiated ice. Using the above assumptions about Europa’s environment, both H$_2$O + O$_2$ and O$_2$/H$_2$O mixtures on Europa could form a detectable steady-state concentration of H$_2$O$_2$; a mixture of H$_2$O + CO$_2$ would not, for an assumed lifetime of 100 days. Obviously the proper choice of $G$ requires knowledge of the composition of the ice on Europa. If H$_2$O + CO$_2$ is an important contributor to the H$_2$O$_2$ concentration, adjustments to the model will be required. For example, the steady-state abundance increases by decreasing
TABLE II

Observed Band Position for H₂O₂ in the 3.5-μm Region

<table>
<thead>
<tr>
<th>Observation of H₂O₂</th>
<th>Conditions</th>
<th>H₂O₂ peak position in the 3.5-μm region</th>
<th>FWHM (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europa spectrum&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>2857 ± 12, 3.50 ± 0.015</td>
<td>~0.06</td>
</tr>
<tr>
<td>Laboratory results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O + H₂O₂ (100 : 13)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Diffuse reflection IR, 300 K liquid cooled to 80 K</td>
<td>2854, 3.504</td>
<td>~0.06</td>
</tr>
<tr>
<td>H₂O, UV photolysis&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Transmission IR, 10 K, Warmed to 70 K</td>
<td>2860, 3.496</td>
<td>0.08</td>
</tr>
<tr>
<td>Laboratory results, this paper</td>
<td>Transmission IR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O + O₂, p⁺ irr.</td>
<td>T = 80 K</td>
<td>2841, 3.50</td>
<td>0.15</td>
</tr>
<tr>
<td>O₂/H₂O, p⁺ irr.</td>
<td>T = 80 K</td>
<td>2851, 3.508</td>
<td>0.10</td>
</tr>
<tr>
<td>H₂O + CO₂, p⁺ irr.</td>
<td>T = 80 K</td>
<td>2851, 3.508</td>
<td>0.12</td>
</tr>
<tr>
<td>H₂O, p⁺ irr.</td>
<td>T = 18 K</td>
<td>2856, 3.501</td>
<td>0.06</td>
</tr>
<tr>
<td>Warmed to 120 K</td>
<td>2855, 3.500</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Warmed to 80 K</td>
<td>2854, 3.504</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Warmed to 160 K</td>
<td>2845, 3.515</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>H₂O + H₂O₂ (100 : 1.4)</td>
<td>T = 18 K</td>
<td>2843, 3.517</td>
<td>0.12</td>
</tr>
<tr>
<td>Warmed to 80 K</td>
<td>2841, 3.520</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Warmed to 160 K</td>
<td>2842, 3.519</td>
<td>0.07</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Carlson et al. (1999).
<sup>b</sup> Gerakines et al. (1996).
<sup>c</sup> Gerakines (pers. commun.).

The density of radicals formed in an individual event increases with the stopping power of the ion. Since radical–radical reactions are more important as the stopping power of the incident radiation rises, we expect our yield of H₂O₂ to be greater than in γ- and X-ray experiments, but perhaps lower than in α irradiations. Since HO₂ is reported (Swallow 1973) to be one of the primary products in ion irradiated ices, then we expect HO₂ to be formed in our proton irradiated ices due to the high stopping power of the proton. The reaction normally invoked to explain HO₂ formation involves the destruction of peroxyde:

\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2. \]  

The most striking result in our work is probably the lack of H₂O₂ at 80 K in irradiated H₂O ice. Most likely, peroxyde is made at 80 K, but its concentration is below our IR detection limit, which is about 0.1 mol%. It is difficult to decide upon one single mechanism to explain why H₂O₂ is seen in our irradiated amorphous H₂O ices at 16 K but not at 80 K. One possibility is that reaction (4) may be more efficient at removing H₂O₂ at 80 K than at 16 K. A second possibility is that hydrogen molecules may play a role in limiting reaction (4) at 16 K by reacting with the destruction rate, or by assuming smaller ice densities (our calculations and those of Carlson et al. (1999) are based on an ice density of 1 g cm⁻³). Alternatively, a model in which more H₂O₂ is concentrated in the top few tens of micrometers of the ice, instead of averaged over the range of the most penetrating particle (180 μm for electrons), would increase the percentage abundance detected. The proper value of G also needs to include any contributions from electrons and heavy ions whose energy fluxes are about the same as for protons.

(c) Formation Mechanisms for H₂O₂

In our experiments, the initial radiation effect is the creation of ionization and excitation events in an ice along the tracks of the incident protons. Ionization of molecules will produce electrons which may either enter into chemical reactions or, given sufficient energy, form a separate track of radiation events. In H₂O, both H and OH radicals are formed during radiolysis and can undergo radical–radical reactions to reform H₂O and to make H₂ and H₂O₂:

\[ \text{H} + \text{OH} \rightarrow \text{H}_2\text{O} \]  
\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]  
\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2. \]
OH radicals:

\[
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}.
\] (5)

In other words, reactions (4) and (5) may compete for “free” OH radicals. Because H\textsubscript{2} is removed by sublimation at 80 K, then more OH will be available for reaction (4) at 80 K than at 16 K, lowering the observed H\textsubscript{2}O\textsubscript{2} abundance.\(^1\) A third possibility is that reaction (1), reformation of H\textsubscript{2}O, is more efficient at 80 K than at 16 K, lowering the H\textsubscript{2}O\textsubscript{2} yield at the higher temperature. Evidence for an enhancement of reaction (1) near 80 K relative to 16 K is provided by experiments on the radiation amorphization of crystalline H\textsubscript{2}O ice (Moore and Hudson 1992). Ice at 77 K shows a much greater resistance to amorphization than at 16 K, apparently due to the higher efficiency of the H + OH reaction. In the absence of additional data, it is difficult to decide which, if any, of these mechanisms is the most important. Reactions (1)–(5) may well be simplifications of processes involving solid-state defects in ices, but these reactions are thought to reflect the proper stoichiometry.

As an alternative to the above mechanisms, we also have considered the reaction of H\textsubscript{2}O\textsubscript{2} with electrons produced by the incident radiation:

\[
e^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-.
\] (6)

At room temperature, destruction of H\textsubscript{2}O\textsubscript{2} by this reaction is orders of magnitude faster than either reaction (4) or reaction (5). Since electron trapping in ice is expected to be smaller at 80 K than 16 K, more \(e^-\) will be available at the higher temperature for reaction with H\textsubscript{2}O\textsubscript{2} by reaction (6). This is consistent with the absence of H\textsubscript{2}O\textsubscript{2} from the spectra of H\textsubscript{2}O ice irradiated at 80 K. Reaction (6)’s importance in our ices was examined in two separate experiments at 80 K involving efficient electron “scavengers,” namely CO\textsubscript{2} and N\textsubscript{2}O. Although pure H\textsubscript{2}O ice irradiated at 80 K did not show H\textsubscript{2}O\textsubscript{2}, when either an H\textsubscript{2}O + CO\textsubscript{2} or H\textsubscript{2}O + N\textsubscript{2}O ice was irradiated at 80 K, H\textsubscript{2}O\textsubscript{2} was clearly seen. Our interpretation is that in the later two cases, CO\textsubscript{2} and N\textsubscript{2}O consumed some of the available electrons, protecting them from destroying \( \cdot \text{H}_2\text{O}_2 \) by reaction (6). The result was a greater yield of H\textsubscript{2}O\textsubscript{2}, which was reflected in the increase in the H\textsubscript{2}O\textsubscript{2} band strength. These experiments demonstrate that an electron scavenger can influence H\textsubscript{2}O\textsubscript{2} abundances in irradiated ices and may explain changes in H\textsubscript{2}O\textsubscript{2} abundances with temperature.

The formation of H\textsubscript{2}O\textsubscript{2} in H\textsubscript{2}O ice having O\textsubscript{2} either mixed in or adsorbed on its surface is perhaps easier to understand. We have previously shown that H-atom addition reactions result during proton irradiation of H\textsubscript{2}O + C\textsubscript{2}H\textsubscript{2}, forming C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} (Moore and Hudson 1998), and during irradiation of H\textsubscript{2}O + CO, forming H\textsubscript{2}CO and H\textsubscript{2}CH\textsubscript{2}OH (Hudson and Moore 1999). H-atom addition to O\textsubscript{2} to form H\textsubscript{2}O\textsubscript{2} should proceed with little difficulty. Radiolysis generates H atoms from H\textsubscript{2}O which may then add sequentially to O\textsubscript{2} to make peroxide:

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2,
\] (7)

\[
\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2.
\] (8)

Our experiment with H\textsubscript{2}O + \textsuperscript{18}O\textsubscript{2} is consistent with these reactions since it showed that H\textsubscript{2}\textsuperscript{18}O\textsubscript{2} was formed (see Results, Section f). This identification was supported by numerous experiments which compared the position of H\textsubscript{2}O\textsubscript{2} in irradiated H\textsubscript{2}\textsuperscript{16}O, H\textsubscript{2}\textsuperscript{18}O, H\textsubscript{2}\textsuperscript{16}O + \textsuperscript{16}O\textsubscript{2}, and H\textsubscript{2}\textsuperscript{18}O + \textsuperscript{18}O\textsubscript{2} ices. An alternative to reaction (7) is that O\textsubscript{2} may capture electrons to form O\textsubscript{2}\textsuperscript{-} which is then protonated to make HO\textsubscript{2}, followed by reaction (8) to peroxide.

We also have observed O\textsubscript{3} formation in experiments on ice samples made from O\textsubscript{2} and H\textsubscript{2}O. The simplest ways that O\textsubscript{3} can be made are probably O-atom addition,

\[
\text{O}_2 \rightarrow \text{O} + \text{O}.
\] (9)

\[
\text{O}_2 + \text{O} \rightarrow \text{O}_3,
\] (10)

or O-atom transfer from a hydroxyl radical,

\[
\text{OH} + \text{O}_2 \rightarrow \text{H} + \text{O}_3.
\] (11)

Our experiment with a H\textsubscript{2}\textsuperscript{16}O + \textsuperscript{18}O\textsubscript{2} mixture confirmed that both \textsuperscript{18}O\textsubscript{2} and \textsuperscript{16}O\textsubscript{18}O\textsubscript{2} are formed, as predicted by reactions (9)–(11). These results concerning O\textsubscript{3} will be presented in a future paper.

Finally, peroxyde was observed at both 16 and 80 K in our radiation experiments with H\textsubscript{2}O + CO\textsubscript{2} ice. It is likely that CO\textsubscript{2} scavenges electrons, protecting H\textsubscript{2}O\textsubscript{2} from destruction at 80 K by reaction (6). This agrees with our H\textsubscript{2}O + C\textsuperscript{18}O\textsubscript{2} experiment: the H\textsubscript{2}O\textsubscript{2} synthesized was at the same IR position as H\textsubscript{2}O\textsubscript{2} made from the H\textsubscript{2}O + C\textsuperscript{18}O\textsubscript{2} mixture. Additional support for this mechanism comes from our experiments at 16 and 80 K with N\textsubscript{2}O, an efficient electron scavenger. Irradiated H\textsubscript{2}O\textsubscript{2} + N\textsubscript{2}O ices always showed a peroxyde band, as expected if N\textsubscript{2}O protects H\textsubscript{2}O\textsubscript{2} from destruction at the higher temperature. Clearly additional experiments are needed, perhaps with H\textsubscript{2}\textsuperscript{18}O or with other electron scavengers such as SF\textsubscript{6}.

In conclusion, our work demonstrates that H\textsubscript{2}O\textsubscript{2} is not produced in proton-irradiated H\textsubscript{2}O ice at 80 K in sufficient abundance for IR detection. However, we have also shown that adding O\textsubscript{2} or CO\textsubscript{2} to the ice will raise the abundance of H\textsubscript{2}O\textsubscript{2} to where it can be observed in the infrared. Our results suggest that the presence of O\textsubscript{2} in H\textsubscript{2}O ice will produce detectable concentrations of H\textsubscript{2}O\textsubscript{2} for the radiation environment of Europa discussed by Carlson et al. (1999). If, however, CO\textsubscript{2} is an important ice component on Europa, then adjustments to some of the modeled parameters will be required. Since Ganymede and Callisto receive only 7 and 0.2%, respectively, of the energy flux received by Europa, the steady-state concentrations of H\textsubscript{2}O\textsubscript{2} on those satellites will be correspondingly lower than on Europa, placing the

\(^1\) H atoms may react with H\textsubscript{2}O\textsubscript{2} in a reaction similar to (4).
H$_2$O$_2$ IR band’s intensity below the level of detection. (This assumes that the same models and ice mixtures apply to Ganymede and Callisto as to Europa). Finally we note that our results are based on proton radiolysis, protons being a major component of the jovian radiation environment. This environment also includes $e^-$, Sn$^+$, and O$^{1+}$, and additional experiments will be required to understand the role of each species in forming H$_2$O$_2$.

ACKNOWLEDGMENTS

The authors gratefully acknowledge R. W. Carlson for sending us a preprint describing the detection of H$_2$O$_2$ on Europa and for a copy of the NIMS IR data. We also benefited greatly from numerous discussions with R. E. Johnson. We thank J. F. Cooper for a preprint analyzing the plasma energy flux incident on the Galilean satellites. We acknowledge the cooperation of Steve Brown and Claude Smith of Goddard’s Radiation Facility who operated the Van de Graaff accelerator. This research is supported by NASA through RTOPs 344-33-01 and 344-02-57.

REFERENCES


