Note

Low-temperature thermal reactions between SO₂ and H₂O₂ and their relevance to the jovian icy satellites

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A B S T R A C T

Here we present first results on a non-radiolytic, thermally-driven reaction sequence in solid H₂O + SO₂ + H₂O₂ mixtures at 50–130 K, which produces sulfate (SO₄²⁻), and has an activation energy of 53 kJ/mole. We suspect that these results may explain some of the observations related to the presence and distribution of H₂O₂ across Europa’s surface as well as the lack of H₂O₂ on Ganymede and Callisto.

1. Introduction

The radiation-driven chemistry of surface and near-surface ices of Europa has been studied by several research groups in recent years. In contrast, thermally-driven reactions in outer Solar System ices have remained relatively unexplored. In this note we report new laboratory experiments demonstrating that a straightforward sequence of hydrolysis, protonation, and redox chemistry can convert SO₂ into SO₄²⁻ (sulfate) at the temperatures of Europa’s surface and in the presence of H₂O₂ (hydrogen peroxide), a well-known radiation product of H₂O–ice. These reactions suggest that sub-surface SO₄²⁻ formation will occur in the absence of the direct reach of jovian magnetospheric radiation.

Laboratory studies of H₂O–ice, one of the more abundant substances on cold surfaces in outer space, have shown that radiation can cause both amorphization of crystalline H₂O–ice (Hudson and Moore, 1995; Strazzulla et al., 1992) and the production of new molecules, such as H₂O₂, H₂, and O₂. Of these three species, H₂O₂ (hydrogen peroxide) formation has been observed in situ by laboratory infrared (IR) spectroscopy in H₂O–ice irradiated at temperatures relevant to extraterrestrial surfaces (Loeffler et al., 2006a; Moore and Hudson, 2000; Zheng et al., 2006). Although all of these prior studies showed that the H₂O₂ abundance is relatively low in irradiated H₂O–ice, the H₂O₂ absorption at 3.5 μm is well-separated from the stronger OH stretching vibrations of water, making it an attractive candidate for observation on planetary surfaces if both H₂O–ice and radiation are present.

Given the many extraterrestrial objects with surficial H₂O–ice exposed to radiation, one might expect to find H₂O₂ on a great number of icy bodies. However, H₂O₂ has been detected unequivocally only on Europa (Carlson et al., 1999), with IR spectra of Ganymede and Callisto failing to show the 3.5-μm peroxide band. Interestingly, ultraviolet spectra of Ganymede do show O₃ (Noll et al., 1996), a reliable indicator of radiation processing of H₂O–ice containing O₂. Differences exist among surface environments of Europa, Ganymede, and Callisto, such as concerning radiation flux, average surface temperature, and composition, but so far none of these factors readily explains why Europa would be the only place where H₂O₂ is present.

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In recent years we have used IR spectroscopy to investigate the solid-phase radiation chemistry of H₂O + SO₂ ices (Moore et al., 2007), solid sulfuric acid, and sulfuric acid hydrates (Loeffler and Hudson, 2012; Loeffler et al., 2011), all at temperatures relevant to the icy jovian satellites. With H₂O + SO₂ ices, it was observed that radiation readily produces SO₄²⁻ (sulfate ion), presumably by the oxidizing action of radiolytically-generated H₂O₂. This assumption has been tested in the present paper by studying IR spectra of unirradiated H₂O + SO₂ + H₂O₂ ices as they are warmed. We have observed that even at relatively low temperatures, H₂O₂ and SO₂ react thermally in the presence of H₂O–ice. The main products of the reaction have been identified and the reaction’s rate has been measured at 110–122 K, temperatures found on the jovian icy satellites mentioned above.

2. Experimental methods

Experiments were performed with a cryostat (Tmax ~ 10 K) operating in a stainless steel high-vacuum chamber (P ~ 1 x 10⁻⁷ Torr). Ice films were prepared by codeposition of H₂O, H₂O₂, and SO₂ onto a pre-cooled (50–100 K) gold-coated aluminum mirror using three separate pre-calibrated gas lines. Pure H₂O₂ was prepared in a glass manifold, using the technique described previously (Loeffler and Baragiola, 2011). During deposition, the sample’s thickness was monitored with interferometry using a diode laser (670 nm). In all experiments the thickness of the resulting H₂O + SO₂ + H₂O₂ (80:14:6) ice was 1.3 ± 0.3 μm, assuming indices of refraction at 670 nm are similar to those measured in the visible region, 1.31 for H₂O (Merwin, 1930), 1.4 for H₂O₂ (Giguère, 1943) and 1.36 for SO₂ (Musso et al., 1983) uniform mixing, and an ice density of 0.96 g/cm³ (0.82 g/cm³ for H₂O (Westley et al., 1998), 1.6 g/cm³ for H₂O₂ (Loeffler et al., 2008b) and 1.49 g/cm³ for SO₂ (Westley, 1983). Each sample’s IR spectrum was recorded before, during, and after warming at 1 K/min to the annealing temperature (110–130 K). Spectra of ices were measured from 7000 to 400 cm⁻¹ with a Bruker Vector Fourier Transform infrared spectrometer at 2-cm⁻¹ resolution and with 200-scan accumulations. To obtain a spectrum, the reflectance from the ice-coated substrate was ratioed against the reflectance of the bare substrate, taken before ice formation, and then converted to absorbance units.
To quantify the kinetics of the thermal reactions occurring in our samples, we first fit the baseline of the 2850 cm\(^{-1}\) overtone band of H\(_2\)O with a non-linear curve and then integrated this same H\(_2\)O IR feature. We chose to examine H\(_2\)O and not SO\(_2\) because the sublimation of pure H\(_2\)O\(_2\) is negligible below 130 K, whereas the sublimation of pure SO\(_2\) can become significant above 100 K, the temperature region of interest. We note that when H\(_2\)O\(_2\) is dispersed in water the strength of the 2850 cm\(^{-1}\) dependence was confirmed in H\(_2\)O–H\(_2\)O\(_2\) calibration experiments and we made use of it in our calculations; the strength of the H\(_2\)O\(_2\) band in question drops linearly by about 20\% between 50 and 130 K.

3. Results

Fig. 1 shows the IR spectrum of an H\(_2\)O + SO\(_2\) + H\(_2\)O\(_2\) (80:14:6) ice after deposition at 50 K, during warming to 118 K, and while held at 118 K. At 50 K, each of the three molecules of the sample is easily identified in this spectral region: H\(_2\)O (3625 cm\(^{-1}\)), H\(_2\)O (1655 cm\(^{-1}\)), and SO\(_2\) (1329 and 1151 cm\(^{-1}\)). On warming to 118 K, new absorptions, belonging to HSO\(_3\) (1035 cm\(^{-1}\)), SO\(_2\)\(_2\) (1092 cm\(^{-1}\)), and SO\(_2\) (954 cm\(^{-1}\)) appeared, as did a broadening on the high-wavenumber side of the H\(_2\)O band at 1655 cm\(^{-1}\), indicating H\(_2\)O\(_2\) formation. As the sample was annealed at 118 K, the main SO\(_2\)\(_2\) band continued to increase, other weaker bands of SO\(_2\) (605 cm\(^{-1}\) and 980 cm\(^{-1}\)) appeared, and the H\(_2\)O and SO\(_2\) bands decreased significantly. Fig. 2 shows the H\(_2\)O\(_2\) abundance in the sample as a function of time (50 K; t = 0) for annealing temperatures of 110, 118, and 130 K. In all cases the H\(_2\)O\(_2\) abundance began to decrease around 100 K and continued to fall as the sample was annealed.

For the samples held at 110 and 118 K, the H\(_2\)O\(_2\) abundance dropped by a factor of two and a factor of eight, respectively, after 1200 min, while only ~20 min were needed at 130 K for the H\(_2\)O\(_2\) abundance to drop below the noise level. Blank experiments with H\(_2\)O–H\(_2\)O\(_2\) showed that over these same time periods there was no H\(_2\)O\(_2\) loss, as expected from the negligible sublimation rate of H\(_2\)O\(_2\) at 130 K.

The inset of Fig. 2 shows an Arrhenius plot derived from six different annealing temperatures, which together yielded an activation energy of 53 ± 5 kJ/mole. The rate constant, k, was derived from N = N\(_0\)exp(−kt), since we observed that, to a first approximation, the H\(_2\)O\(_2\) abundance (N) dropped exponentially with time (t) at each temperature studied. In the higher temperature reactions, the reaction began before we reached the annealing temperature, so in all cases we calculated k by equating it to ln(2)/(t\(_{1/2}\)), where t\(_{1/2}\) is the time at the annealing temperature needed for the H\(_2\)O\(_2\) abundance to drop to half of its original value. We note that as the abundance of H\(_2\)O\(_2\) has already dropped by a factor of two by the time we warm to ~125 K (see 130 K experiment in Fig. 2), we only used annealing temperatures below 122 K to calculate the activation energy. The error that we give in the activation energy is a combination of the difficulty of fitting the H\(_2\)O\(_2\) baseline, the narrow temperature range (12 K) for which we can obtain a value for t\(_{1/2}\), and the fact that at the upper temperatures the reactions already have proceeded to some extent by the time the sample attained those temperatures. Future studies will focus on reducing the uncertainty in these measurements by extending the experiments to lower temperatures so that the activation energy can be more-confidently used below 100 K.

4. Discussion

4.1. Reaction chemistry

Thermal reactions between SO\(_2\) and H\(_2\)O have been studied extensively within the atmospheric-chemistry community due to the importance of such chemistry in removing SO\(_2\), in liquid, gas, and solid phases, from Earth’s atmosphere. The primary reaction sequence is believed to begin with the formation of bisulfite (HSO\(_3\)) through (1)

\[
H_2O + SO_2 \rightarrow HSO_3 + H^+ \tag{1}
\]

where the H\(^+\) either rapidly or in concerted fashion attaches to a second H\(_2\)O molecule to form hydronium:

\[
H^+ + H_2O \rightarrow H_3O^+ \tag{2}
\]

In our previous studies with H\(_2\)O + SO\(_2\) ices, we found that these thermal reactions occur in the solid state even at temperatures below 100 K (Loeffler and Hudson, 2010). We now find, in addition, that in the presence of H\(_2\)O\(_2\) the bisulfite is oxidized to form the sulfate (SO\(_4^{2-}\)) ion (Martin and Damschen, 1981):

\[
H_2O + HSO_3 \rightarrow SO_4^{2-} + H^+ \tag{3}
\]

Fig. 1 provides evidence that these same thermally-induced reactions occur in our H\(_2\)O + SO\(_2\) + H\(_2\)O\(_2\) ices. Beginning with the 50-K spectrum and working toward those for higher temperatures, IR absorptions of both HSO\(_3\) (1035 cm\(^{-1}\)) and SO\(_2\)\(_2\) (1092 cm\(^{-1}\)) products can be seen starting at ~80 K during warming. Both bands continued to increase with temperature until the SO\(_2\)\(_2\) feature was one of the more-prominent remaining IR absorptions. The increase in abundances for the HSO\(_3\) and SO\(_2\)\(_2\) ions correlated with the decrease in absorption band areas of reactants SO\(_2\) and H\(_2\)O\(_2\) (Fig. 1), supporting the simple reaction sequence already described. Comparing the H\(_2\)O\(_2\) loss for our different annealing temperatures, we see that not surprisingly the reaction proceeds the fastest at the highest temperature. However, even at the lower temperatures, the H\(_2\)O\(_2\) abundance is still decreasing after the longest times studied (~1200 min), indicating that given enough time all of the H\(_2\)O\(_2\) will convert to SO\(_2\)\(_2\) via reaction (3).

4.2. Icy satellite implications

Infrared spectra of the surface of Europa, Ganymede, and Callisto all contain an absorption at 4.05 \(\mu\)m, which usually is assigned to SO\(_2\) (Hansen and McCord, 2008; Hibbitts et al., 2000; McCord et al., 1998). In contrast, the 3.5-\(\mu\)m band of H\(_2\)O\(_2\) has been found only in Europa’s spectra (Carlson et al., 1999; Hansen and McCord, 2008). Our experiments show that the abundance of H\(_2\)O\(_2\) in these surface ices depends on the presence of SO\(_2\), and that, conversely, sulfur dioxide’s abundance will be influenced by the presence of H\(_2\)O\(_2\). Given these new laboratory results, we now turn to some of the previous observations of the jovian icy satellites.

On Europa, although both H\(_2\)O\(_2\) and SO\(_2\) have been detected they do not appear to be uniformly distributed. Hansen and McCord (2008) determined that the SO\(_2\) infrared feature was present on Europa’s trailing hemisphere. This agrees with previous measurements of Europa’s ultraviolet reflectance spectrum (Domingue and Lane, 1998; Hendrix et al., 2011; Hendrix and Johnson, 2008; Lane et al., 1981), which showed a strong slope on the moon’s trailing side, attributed to SO\(_2\) (0.28 \(\mu\)m band center). It also is consistent with the sulfur implantation rate being an order of magnitude higher on Europa’s trailing hemisphere (Johnson et al., 2004),
Interestingly, the more-recent ultraviolet measurements indicate that SO$_2$ is not only more abundant on the trailing side but that it is actually absent on the leading side, where the majority of the H$_2$O$_2$ detections have been made (Carlson et al., 1999). Thus, based on our results it seems plausible that the distribution of SO$_2$ and H$_2$O$_2$ may be a result of excess SO$_2$ consuming any H$_2$O$_2$ produced by radiolysis in the trailing hemisphere and excess H$_2$O$_2$ consuming the SO$_2$ formed by implantation in the leading hemisphere. Finally, we point out that one recent study did detect both H$_2$O$_2$ and SO$_2$ in a spectrum of an ice-rich region on Europa's trailing side (Hansen and McCord, 2008). However, it is possible that these two molecules may be spatially separated, but sufficiently close to lie within the same pixel area of the detector.

On Callisto and Ganymede the 3.5-µm absorption diagnostic of H$_2$O$_2$ is absent, which could indicate that surficial SO$_2$ is widespread or that the H$_2$O$_2$ abundance is simply much lower than on Europa (Hendrix et al., 1999; Hendrix and Johnson, 2008). The former possibility is consistent with IR measurements of Ganymede and Callisto (McCord et al., 1998), which showed that each satellite's spectrum contained the 4.05-µm absorption band attributed to SO$_2$. However, we note that there has been some discussion as to whether another species, such as H$_2$CO$_3$ or other carbonates (Johnson et al., 2004), could provide an adequate match for the 4.05-µm feature in Callisto's spectrum, as this band does not seem to be correlated with magnetospheric bombardment (Hibbitts et al., 2000). Also, the most recent ultraviolet measurements show little variation across Callisto's surface (Hendrix and Johnson, 2008).

As the H$_2$O + SO$_2$ + H$_2$O$_2$ reaction we studied occurs quickly at temperatures relevant to these icy satellites ($1$–$1.5$ yr at $100$ K and $0.3$ h at $120$ K), we expect that it plays an important role in the evolution of the jovian icy satellites' surface chemistry and may explain observations of Europa related to the presence and distribution of H$_2$O$_2$ as well as the lack of H$_2$O$_2$ on Ganymede and Callisto. If other molecules prove to be reactive with H$_2$O$_2$ at these or even lower temperatures, then similar thermal chemistry may explain why H$_2$O$_2$ has not been detected on most Solar System icy bodies exposed to radiation. Future laboratory studies will focus on extending the reported measurements to other temperatures and concentrations, identifying and quantifying other thermal reactions that may occur between H$_2$O$_2$ and other astrochemically-relevant molecules, and establishing whether the reaction products contain IR absorptions which could be detected by remote sensing. Finally, we note that the reactions we have described are not restricted to the surface of Europa and other worlds. To the extent that vertical transport of radiolytic products occurs (Greenburg, 2010), our reactions (1)–(3) also will take place beneath the IR-sensed layer of Europa, providing a thermally-driven source of SO$_2^-$.

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References


