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Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions

Mark J. Loeffler[1] and Reggie L. Hudson[1,2]

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[1] Laboratory experiments have demonstrated that magnetospheric radiation in the Jovian system drives reaction chemistry in ices at temperatures relevant to Europa and other icy satellites. Here we present new results on thermally-induced reactions at 50–100 K in solid H_2O-SO_2 mixtures, reactions that take place without the need for a high-radiation environment. We find that H_2O and SO_2 react to produce sulfur oxyanions, such as bisulfite, that as much as 30% of the SO_2 can be consumed through this reaction, and that the products remain in the ice when the temperature is lowered, indicating that these reactions are irreversible. Our results suggest that thermally-induced reactions can alter the chemistry at temperatures relevant to the icy satellites in the Jovian system. **Citation:** Loeffler, M. J., and R. L. Hudson (2010), Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions, *Geophys. Res. Lett.*, *37*, L19201, doi:10.1029/2010GL044553.

1. Introduction

[2] Numerous laboratory studies by our group and others [e.g., *Moore and Hudson*, 2000; *Gomis et al.*, 2004; *Loeffler et al.*, 2006] have demonstrated that magnetospheric radiation in the Jovian system can drive chemical and physical changes in the surface ice of satellites such as Europa. In contrast, it does not appear to be widely recognized that thermally-induced reactions also can occur in ices at temperatures on the order of 80 K even if radiation is not present. Here we report recent experiments on one such set of reactions, namely those involving H_2O and SO_2, two molecules that are believed to be present on Europa, Ganymede, and Callisto [*Lane et al.*, 1981; *McCord et al.*, 1998a].

[3] Remote sensing of the Jovian satellites has revealed and helped to identify surface materials including H_2O ice [*Kuiper*, 1957; *Johnson and McCord*, 1971], SO_2 [*Lane et al.*, 1981], CO_2 [*Hansen and McCord*, 2008], H_2O_2 [*Carlson et al.*, 1999a], O_2 [*Calvin et al.*, 1996], O_3 [*Noll et al.*, 1996], and hydrated materials [*Carlson et al.*, 1999b; *McCord et al.*, 1998b]. Formation of some of these species is readily explained by low-temperature radiolysis of ices. For example, it has been shown that the H_2O_2 abundance derived from Galileo-NIMS data is consistent with what is expected from a consideration of the Jovian radiation environment and laboratory work on the radiation chemistry of H_2O [*Carlson et al.*, 1999a]. More-recent experiments by *Moore et al.* [2007] with H_2O + SO_2 ices demonstrated that their radiolysis at 86 – 132 K produces hydronium (H_3O^+) and sulfate (SO_4^{2-}) ions that, after warming under vacuum to remove water, yield $H_2SO_4 \bullet H_2O$. Similar experiments with H_2O + H_2S ices led to $H_2SO_4 \bullet 4\ H_2O$. The low-temperature observation of H_3O^+ and SO_4^{2-}, as opposed to H_2SO_4, was in keeping with the strongly-acidic nature of the latter and the high abundance of H_2O molecules in the ice.

[4] Although the low temperatures of the icy Jovian satellites give little hope for purely thermal chemistry, thermodynamic equilibrium constants (denoted *K*) nevertheless are suggestive. The acid-base reaction between H_2O and CO_2, two molecules widely observed in solar system ices, is

$$2\ H_2O + CO_2 \rightarrow H_3O^+ + HCO_3^- \qquad (1)$$

with $K \sim 10^{-7}$ near room temperature [*Soli and Byrne*, 2002]. While this value cannot be uncritically applied to cryogenic temperatures, it does suggest that purely-thermal formation of HCO_3^- is unlikely at ~100 K in H_2O-ice. In agreement with this, none of the earlier papers on H_2O + CO_2 ices [e.g., *Sandford and Allamandola*, 1990; *Hudson and Donn*, 1991] reported ion formation. This low equilibrium constant contrasts strongly with the high degree of ionization for the strong acid H_2SO_4 in water, with $K \sim 10^3$ for

$$H_2O + H_2SO_4 \rightarrow H_3O^+ + HSO_4^- \qquad (2)$$

and a substantial subsequent dissociation of HSO_4^- into SO_4^{2-} [*Williams and Fraústo da Silva*, 2000; *Lund Myhre et al.*, 2003]. Correspondingly, our recent ice experiments, described above, showed H_3O^+, HSO_4^-, and SO_4^{2-}, but no detectable H_2SO_4 until the water was removed [*Moore et al.*, 2007].

[5] We now consider a case intermediate between H_2O + CO_2 and H_2O + H_2SO_4 ices, namely solid-phase mixtures of H_2O and SO_2. Sulfur dioxide in aqueous solution reacts according to

$$2\ H_2O + SO_2 \rightarrow H_3O^+ + HOSO_2^- \left(\text{and/or } HSO_3^-\right) \qquad (3)$$

with $K \sim 10^{-2}$ [*Scott and Hobbs*, 1967], which suggests that this reaction might be observed in ices. Therefore, in the experiments described here we have used infrared (IR) spectroscopy to study solid H_2O + SO_2 mixtures at temperatures that are relevant to the icy Jovian satellites. We

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[1] Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

[2] Department of Chemistry, Eckerd College, St. Petersburg, Florida, USA.

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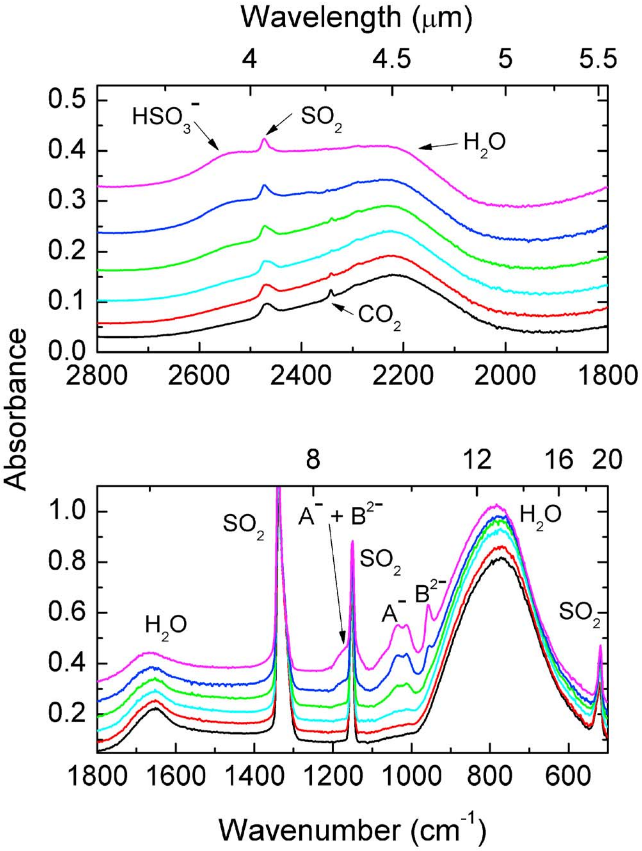

Figure 1. Infrared spectra of $H_2O + SO_2$ (6:1) mixtures, deposited at (from bottom to top in each panel) 50, 60, 70, 80, 90, and 100 K. $A^- = HSO_3^-$ and/or $HOSO_2^-$, or its dimer. $B^{2-} = S_2O_5^{2-}$. The spectra have been vertically offset for clarity.

have determined that reaction (3) given above does indeed produce detectable amounts of ions, and we have quantified their formation as a function of deposition temperature and heating.

2. Experimental Methods

[6] Experiments were performed with a cryostat (T_{min} ~ 10 K) operating in a stainless steel high-vacuum chamber ($P < 1 \times 10^{-7}$ Torr). Ice films were prepared by co-deposition of H_2O and SO_2 onto a pre-cooled (50–100 K) gold-coated aluminum mirror using two separate pre-calibrated gas lines. During deposition, the film thickness was monitored with interferometry using a diode laser (670 nm). In most experiments the resulting ice was 2.5 μm thick and had a molecular number ratio of ~6:1 H_2O:SO_2, assuming indices of refraction at 670 nm of 1.31 for H_2O [*Warren*, 1984] and 1.36 for SO_2 [*Musso et al.*, 2000], uniform mixing, and an ice density of 0.94 g/cm^3 (0.85 g/cm^3 for H_2O and 1.46 g/cm^3 for SO_2). After preparation, each sample's IR spectrum was recorded before, during, and after warming at 0.2 – 1 K/min to as high as 100 K.

[7] Spectra of ices were measured from 7000 to 400 cm^{-1} with a Bruker Vector Fourier Transform infrared spectrometer at 4-cm^{-1} resolution and accumulations of 100 scans. To obtain a spectrum, we ratioed the reflectance from the ice-coated substrate against the reflectance of the bare substrate, taken before ice formation, and converted the result to absorbance units. For additional experimental details see *Hudson and Moore* [2007].

[8] Areas of SO_2 bands were used to determine the relative abundance of this molecule, and were derived after subtraction of the baselines around the ν_1 (1151 cm^{-1}) and ν_3 (1338 cm^{-1}) features. We note that the ν_1 band was more difficult to integrate, due to underlying absorptions that grew in with temperature (e.g., see Figure 1), but that both ν_1 and ν_3 yielded results consistent within 5%.

3. Results

[9] Figure 1 shows IR spectra of $H_2O + SO_2$ (6:1) mixtures at deposition temperatures from 50 to 100 K in the range from 2800 to 500 cm^{-1}. In this region, the spectra are dominated by the ν_3 (1338 cm^{-1}) and ν_1 (1151 cm^{-1}) vibrational modes of SO_2, along with the lattice vibration ν_L (780 cm^{-1}) of H_2O-ice. Figure 1 also shows the $\nu_1 + \nu_3$ (2450 cm^{-1}), $2\nu_1$ (2295 cm^{-1}, weak) and ν_2 (520 cm^{-1}) absorptions for SO_2, as well as the $3\nu_L$ (2223 cm^{-1}) and ν_2 (1649 cm^{-1}) features for H_2O-ice. See earlier work from this laboratory for full IR spectra from 4000 to 400 cm^{-1} [*Moore et al.*, 2007].

[10] Figure 1 (bottom) shows that as the deposition temperature was increased, IR features at 1034 and 1013 cm^{-1} became increasingly prominent, along with an absorbance at 958 cm^{-1} appearing at the higher temperatures. Checks with one-component ices made of H_2O and of SO_2 failed to show any of these three bands, although they did still appear in spectra of $H_2O + SO_2$ mixtures warmed on uncoated aluminum substrates. This showed that the bands forming above ~50 K were due to a reaction between H_2O and SO_2, and not the underlying non-icy material or either ice alone.

[11] Figure 1 (top) shows spectra for the same ices as represented in the lower panel, but in a different spectral region. Again, a new IR band is seen appearing at the higher temperatures, at 2543 cm^{-1} (3.93 μm). We will return to assignments of these IR features later in the Discussion.

[12] In a separate set of experiments, we recorded spectra of $H_2O + SO_2$ (6:1) ices subjected to various annealing cycles. We found that the small features at 1100 – 950 cm^{-1}, seen in Figure 1 on warming the ice, were not removed by recooling the sample, indicating that these features were due to an irreversible thermally-induced change. We also found a close similarity between the IR spectra of an $H_2O + SO_2$ (6:1) ice grown at 100 K and one that was grown at 50 K and then warmed to 100 K.

[13] Other observations were that as a sample's temperature increased, a broad underlying band grew in near the SO_2 feature at 1151 cm^{-1}, and all SO_2 bands decreased in intensity. In a different set of experiments, we held H_2O + SO_2 samples at fixed temperatures for prolonged periods, so as to record the decrease in SO_2 (reactant) bands and the rise of the IR features of products. As an example, Figure 2 shows the fractional change in SO_2 abundance on first warming a sample and then holding it at 100 K for ~3 hours. We note that while most of the SO_2 was retained in our samples during warming to at least 130 K, we did not grow ices above 100 K as the sticking coefficient of SO_2 appeared to decrease rapidly with temperature, making it difficult to produce $H_2O + SO_2$ mixtures of known composition. Experiments also were done with ices containing much less SO_2 (H_2O:SO_2 ~ 30:1), with results similar to those

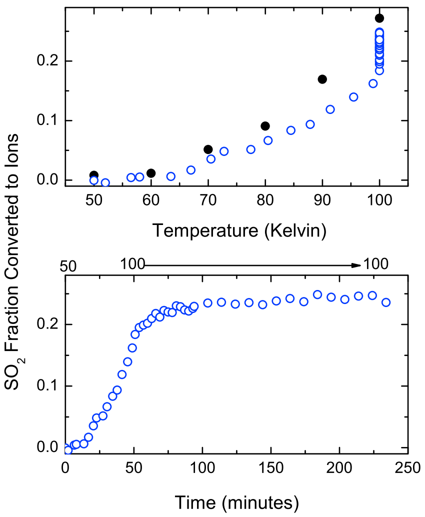

Figure 2. The fraction of SO_2 converted into sulfur oxyanions. (top) The fraction converted as a function of growth temperature (solid circle) and during warming from 50 to 100 K at 1 K/min (open circle). (bottom) The fraction of SO_2 converted as a function of time during warming from 50 to 100 K at 1 K/min.

already described. Adding CO_2 and CH_4 (3–20%) to our $H_2O + SO_2$ ices failed to block the growth of the IR features in the 1100 – 950 cm^{-1} region of Figure 1. Finally, a few $D_2O + SO_2$ ices were studied. The IR features shown growing with temperature in Figure 1 were essentially unchanged by the presence of deuterium.

4. Discussion

[14] Figure 1, and the supporting experiments already described, showed that thermal chemistry took place in our $H_2O + SO_2$ ices. From reaction (3) we expect the formation of bisulfite on warming a $H_2O + SO_2$ mixture, but from there the reaction chemistry becomes complex. Ab initio calculations of *Voegele et al.* [2004] suggest that the initially-formed species in solution should be $HOSO_2^-$, which on further reaction isomerizes to HSO_3^-. Strong support for the latter comes from our observation of a band near 2543 cm^{-1} (3.93 μm) that grows in with temperature. A similar band has been assigned to the SH stretch in HSO_3^- by others [*Connick et al.*, 1982; *Hisatsune and Heicklen*, 1975]. The two features in the 1100 – 1000 cm^{-1} region of Figure 1 resemble the bisulfite bands shown in papers of *Ermatchkov et al.* [2005, Figure 1], and *Zhang and Ewing* [2002, Figure 3], and *Pichler et al.* [1997, Figure 1].

[15] All of these earlier papers support an assignment of the 1034 and 1013 cm^{-1} features of Figure 1 to the S-O stretching vibrations of the two forms of the bisulfite anion, $HOSO_2^-$ and HSO_3^-, although it is difficult to say which band corresponds to which anion. Assigning these features to S-O stretching vibrations is also consistent with the $D_2O + SO_2$ ices we studied, since these same bands were unaffected by the presence of deuterium. An alternative assignment, proposed by *Zhang and Ewing* [2002], suggests that our 1034 feature may be a superposition of absorptions from both anions, while the 1013 cm^{-1} band may be from a bisulfite dimer. The 958-cm^{-1} feature in Figure 1 agrees with the position of the most intense band of pyrosulfite ($S_2O_5^{2-}$, also called metabisulfite and disulfite in the literature). This anion also has a weaker, broader band near 1152 cm^{-1}, which we also observed [see *Ermatchkov et al.*, 2005]. We note that our 958-cm^{-1} feature is not due to SO_3^{2-}, which we observed at 927 cm^{-1} on warming ices made of $H_2O + SO_2 + NH_3$ [*Hisatsune and Heicklen*, 1975].

[16] To summarize, our observations and spectral assignments are consistent with thermal chemistry that converts SO_2 in $H_2O + SO_2$ ices into sulfur oxyanions. Although the precise reaction sequence remains unknown, the following path seems reasonable:

$$SO_2 \rightarrow HOSO_2^- \rightarrow HSO_3^- \rightarrow S_2O_5^{2-} \qquad (4)$$

Formation of $S_2O_5^{2-}$ is possible through

$$2\ HSO_3^- \rightarrow S_2O_5^{2-} + H_2O \qquad (5)$$

or a similar reaction with the other form of bisulfite [*Zhang and Ewing*, 2002], or a reaction involving both isomers. The most-likely positive counter-ion in our ices is hydronium (H_3O^+), with its IR bands obscured by overlap with those of H_2O itself. Comparing the upper and lower traces in Figure 1 (bottom), for before and after anion formation, we find a slight broadening to the left of the H_2O-ice feature at 1650 cm^{-1}, in the region where H_3O^+, and other forms of the hydrated proton, have an IR absorbance [*Kim et al.*, 2002].

[17] To quantify the conversion of SO_2 into ions, we measured the SO_2 present in ice samples as a function of deposition temperature and during heating, and assumed that all SO_2 lost went into ion formation. Results are presented in Figure 2. The upper panel shows that the amount of SO_2 that reacted rose with deposition temperature such that 25 – 30% of the SO_2 had formed sulfur oxyanions by 100 K. Figure 2 also shows that for a $H_2O + SO_2$ sample made at 50 K, the fraction of SO_2 that reacted when the ice was warmed at 1 K/min increased with temperature. By 100 K about 18% of the SO_2 had been converted into ions, and the reaction continued at 100 K until the amount converted reached an equilibrium value of about 25%. Figure 2 (bottom) also shows that at the highest temperature (100 K) of these experiments, SO_2 sublimation from the ice was negligible, indicating that the decrease in SO_2 abundance below 100 K was entirely due to ion formation. The overall result of these measurements is that our $H_2O + SO_2$ ices showed as much as a 30% conversion of SO_2 into ions by the time 100 K was reached. Total ion abundances on the order of a few percent were achieved. Finally, we note that the ion abundance continued to increase as we warmed our samples to ~130 K, at which point the SO_2 band had decreased by 35-40%. However, we cannot discount that a minor amount of the decrease in the SO_2 band area could be due to sublimation, and thus this value is an upper limit for the amount of SO_2 converted to sulfur oxyanions for the concentrations studied here.

[18] Thermal reactions in $H_2O + SO_2$ ices have rarely been mentioned in the literature. In an earlier paper [*Moore et al.*, 2007] we noted IR bands of ions in some of our spectra, without considering their origin and implications. In an older publication by *Fink and Sill* [1984], the mid-IR spectrum of an ice made of $H_2O + SO_2 + CO_2$ (80:19:1.2) was presented

[*Fink and Sill*, 1984, Figure 19]. The bisufite and pyrosulfite bands are clearly seen, but they were neither noted nor discussed.

5. Astrophysical Implications

[19] Discussions of reaction chemistry on Europa and other icy satellites usually emphasize the upper tens of microns of surface material since that is what is sampled by remote sensing techniques. Knowledge of the reaction chemistry below this thin layer is less certain, but theoretical modeling [e.g., *Greenberg*, 2010] suggests that there will be interactions between the surface and subsurface ice, and possibly with the putative ocean.

[20] Our laboratory work strongly suggests that thermally-driven reactions will contribute to the geochemistry of Europa, and other satellites, and at greater depths than radiolysis alone can reach. For the $H_2O + SO_2$ ices presented here, a rich subsurface thermal chemistry not requiring radiation is likely, involving $HOSO_2^-$, its isomer (HSO_3^-), its dimer ($H_2S_2O_6^{2-}$), its hydrolysis product ($S_2O_5^{2-}$), and, in the presence of NH_3, even its conjugate base (SO_3^{2-}). In addition, absorption bands of these products, such as the HSO_3^- band at 3.93 μm, may explain some of the features in spectra of the Jovian satellites [*McCord et al.*, 1997; *Carlson et al.*, 2009], as these ions′ concentrations are significant: as much as 30% of the SO_2 converts into sulfur oxyanions. Furthermore, the time scales for these reactions also are very short, as we have observed that the bisulfite abundance attains equilibrium within an hour of reaching 100 K, a relevant temperature for Europa.

[21] The sulfur oxyanions produced in these thermally-driven reactions could alter Europa's radiolytic sulfur cycle [*Carlson et al.*, 2002]. In addition, they could also change the physical properties of subsurface ice, such as its ability to trap some of the more-volatile species (e.g., O_2 or CO_2), which would in turn affect the transport of oxidants through a satellite's interior. Thus, thermally-driven reactions, such as those presented here, need to be considered in theoretical modeling that aims to understand either the present state or the chemical evolution of the surface or subsurface of the Jovian icy satellites, a topic of importance for future Europa missions [e.g., *Clark et al.*, 2008]. Future laboratory studies will focus on quantifying the effects that these thermally-driven reactions have on the chemical and physical properties of Europa ice analogs, determining if other ices made from astrophysically-relevant molecules exhibit similar behavior, and establishing whether any of the sulfur oxyanion absorptions provide a quality match to features in the spectra of Europa, Ganymede, and Callisto [*McCord et al.*, 1997; *Carlson et al.*, 2009].

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R. L. Hudson and M. J. Loeffler, Astrochemistry Branch, NASA Goddard Space Flight Center, Code 691, Greenbelt, MD 20771, USA. (mark.loeffler@nasa.gov)