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Sulfur chemistry in the wake of comet Shoemaker-Levy 9

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Abstract. A curious and unexpected result of the impact of P/Shoemaker Levy 9 with Jupiter was the production of enormous amounts of molecular sulfur (S_2). Here we show that S_2 is the natural product of disequilibrium chemistry at low pressures in shocked jovian air, its formation a byproduct of hydrogen recombination. The species observed by the HST — S_2, CS_2, and H_2S — imply that the G fragment penetrated the NH_4SH cloud but did not reach the water table. A typical impact within or below the NH_4SH clouds produces about 0.03-0.1 impactor masses of S_2. Because comets are relatively hydrogen-poor, SO_2, not S_2, is the major product of shocking a water-rich comet, while S_2, CS_2, and OCS are major products of a dessicated comet. In all cases we find that as the gas cools S_2 converts to the stable low temperature allotrope S_8, although other chemical fates not modeled here might intervene first.

Introduction

Diatomic sulfur was observed in absorption by the Hubble Space Telescope in the near UV for the large G impact [*Noll et al.,*} 1995]. The observation was made about 10^4 seconds after the impact took place, at the center of the impact site, over a footprint roughly 3000 km across. The reported column abundance was 5×10^{-4} g cm^{-2} [*Noll et al.*, 1995], although this may be an overestimate [*R. Yelle, pers comm.*, 1995]. If the sulfur were uniformly distributed over the entire impact site, a region more than 10^4 km across, the mass of S_2 would be of order 5×10^{14} g. Even if restricted to the somewhat smaller region actually observed, the impact produced some 5×10^{13} g of S_2. These are enormous masses of sulfur. Where did it come from? Why S_2? Why so much? Where did it go?

Model Description

In this paper we address sulfur chemistry in shocked jovian and cometary gas using both an explicitly time-dependent kinetics model and a comprehensive thermochemical equilibrium model, the latter previously developed to study Jupiter at rest [*Fegley and Lodders,* 1994a]. The kinetics model follows the evolving chemical composition of a parcel of gas by directly integrating the network of chemical reactions. At high temperatures and high pressures chemical reactions are fast and the gas very nearly in thermochemical equilibrium. As the parcel cools and/or rarefies the chemistry increasingly lags behind the evolving conditions, and so becomes increasingly disequilibrated. It is often useful to describe the final state as ``quenched"; the frozen disequilibrium approximates the equilibrium abundances at the quench temperature [*Zel'dovich and Raizer,* 1967, pp. 564-571; *Prinn and Fegley,* 1987}; *Zahnle,* 1990].

In an oxygen-poor environment (*i.e.*, dry jovian air) we include 33 chemically active species: H_2, H, C, CH, CH_2, CH_3, CH_4, C_2, C_2H, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6, C_4H, C_4H_2, N, NH, NH_2, NH_3, CN, HCN, N_2, S, S_2, S_3, S_4, S_8, HS, H_2S, CS, CS_2, NS. Photolysis is neglected. With oxygen this list of species is supplemented by O, O_2, OH, H_2O, CO, CO_2, HCO, H_2CO, NO, SO, OCS, SO_2. The latter system is needed to address the chemistry of wet jovian air; it can also be used to approximate the chemistry of cometary material. Reaction rates and sources will be listed elsewhere. Not all the important reactions have measured rates. Unmeasured but plausibly important reactions must be estimated, which leaves considerable scope for error.

The thermochemical equilibrium calculations provide alternative results that are independent of estimated reaction rates. Although the two approaches (kinetic, equilibrium) are not always in complete agreement, they do agree in general, and where they disagree the source of the disagreement can be explained by plausible disequilibrium processes.

Parcel Histories

We consider two kinds of parcel histories. One kind models the explosion and the subsequent expansion of the fireball. The initial shock conditions, mass of shocked material, and expansion velocity are specified to agree with those generated by a strong point explosion. Thereafter the parcel cools adiabatically as it expands. The second kind models the impact of the plume with the atmosphere. In the latter models the pressure is held constant at a low value (of order 1 μbar to 1 mbar), characteristic of pressures in the reentry shock [*Zahnle and Mac Low,* 1995]. Note that a given parcel is generally shocked twice; i.e., a parcel shocked near the impact site is ejected at high velocity and is shocked again when it reenters the atmosphere. Hence the final state of the gas depends on the second shock. Figure 1 shows an illustrative parcel history taken directly from a numerical model.

The fireball. The mass of air M_f shocked to a temperature greater than T' is approximately

$$25\, m_i \left(\frac{2000}{T'}\right) < M_f(>T') < 100\, m_i \left(\frac{2000}{T'}\right). \qquad (1)$$

Eq. 1 assumes an impact velocity of 60 km/s, a mean molecular weight of 2.4, and $\gamma=1.4$. The lower bound approximates the sedov solution for a strong explosion and the upper bound assumes that the energy of the impact is spread uniformly over the entire mass of shocked gas; i.e., the upper bound would apply if the shocked gas were well mixed.

Atmospheric reentry. The mass of air accelerated to a velocity greater than v by a typical SL-9 explosion is [*Zahnle and Mac Low,* 1995]

$$M_r(>v) = 100\, m_i \left(\frac{1\ \text{km/s}}{v}\right)^{\alpha} \qquad (2)$$

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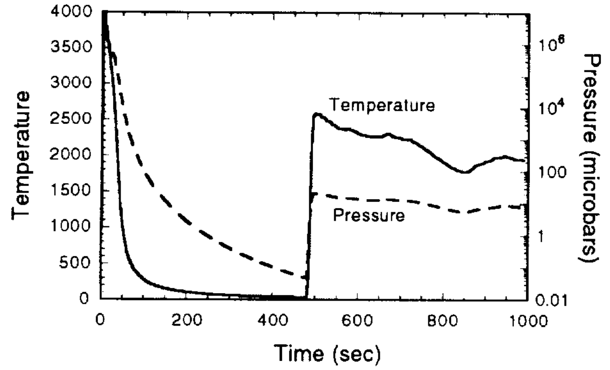

Figure 1. Temperature and pressure history of a representive shocked parcel of jovian air. The parcel originated at the 2 bar level, near the site of the airburst. It was shocked to T>9000 K, expanded, cooled, and ultimately ejected at about 6 km/sec.

where $\alpha \approx 1.5$, and $v<15$ km/s. The peak shock temperature is

$$T' \geq \frac{\gamma-1}{2}\,\frac{m}{k}\,v_z^2 \approx 1500\,\mathrm{K}\left(\frac{\mu}{2.4}\right)\left(\frac{v_z}{5\ \mathrm{km/s}}\right)^2 \qquad (3)$$

where the equality is for a strong shock, and v_z is the normal component of the reentry velocity. T' can be much higher if the gas is polluted with cometary material, because the cometary material raises the mean molecular weight. Material ejected at 5 km/s falls about $r \approx v^2/g \approx 1000$ km from the impact site.

We assume a cooling curve in the reentry shock of

$$T(t) = T'\left(\frac{t_o}{t_o+t}\right)^{1/3} + 120, \qquad (4)$$

where T' denotes the peak shock temperature. We have taken t_o=20 s. It must be emphasized that Eq. 4, while generically representative of real parcels, is essentially an arbitrary construct.

Results

Figure 2 focuses on the sulfur chemistry of a shocked parcel of dry jovian air, as calculated by the kinetics model. The initial chemical composition follows *de Pater* [1991]: compared to solar abundances, carbon is enhanced by a factor of 2.3, nitrogen by 1.5, and sulfur by a factor of 7. There is no water. The temperature and pressure history of the parcel were designed to approximate the history shown in Figure 1.

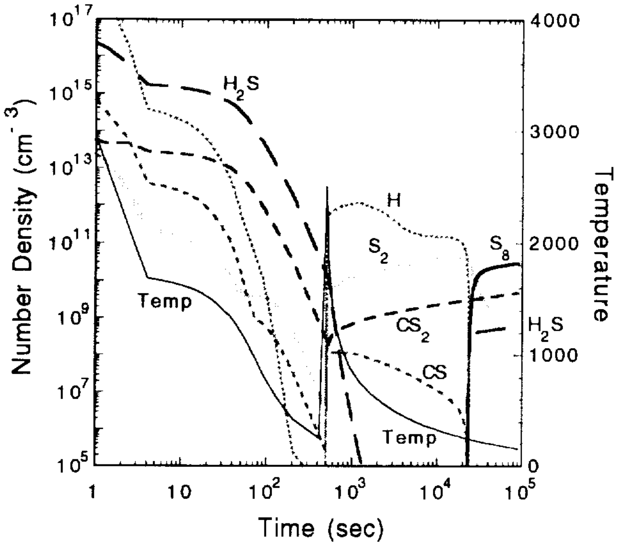

Figure 2. Time-dependent sulfur chemistry in a representive parcel of shocked dry jovian air. The radicals HS and S are omitted for clarity, but H, which drives the disequilibrium chemistry, is shown. Temperature is also shown. The low pressures, here 20 μbars, in the reentry shock strongly favor the disequilibrum production of S_2.

The primary products of the dry fireball are H_2S and CS_2, which are quenched at roughly 1 bar and 2000 K. The high quench temperature and pressure strongly favor the production of H_2S (*c.f.*, Fig. 3). By contrast the radicals H, S, HS, and CS continue to react. In this example essentially all the CS is converted to CS_2. We find that S_2 becomes a major product only for peak shock temperatures exceeding about 10^4 K, for which the quench pressure of an adiabatically expanded parcel is low.

The reentry shock in Fig 2 assumes T'=2500 and a pressure of 10 μ bar. In this particular simulation S_2 is the major sulfur species from 500 to 2×10^4s. As the parcel cools the bulk of the sulfur converts to the stable low temperature allotrope S_8. The period of S_2 dominance is controlled by the cooling timescale and the pressure. At 1 mbar conversion to S_8 occurs at 500 K, at 10 μbar conversion is delayed until T drops to 250 K. At low temperatures the thermodynamically preferred H_2S reappears when atomic hydrogen disappears.

Production of S_2 in a cooling hydrogen-rich gas is driven by the recombination of molecular hydrogen. The key reactions are

$$H + H_2S \rightarrow HS + H_2 \qquad (R1)$$

$$H + HS \rightarrow S + H_2 \qquad (R2)$$

$$S + HS \rightarrow S_2 + H \qquad (R3)$$

All three reactions are exothermic. The net reaction is

$$2H + 2H_2S \rightarrow S_2 + 3H_2$$

The equilibrium increasingly favors the products as the temperature drops.

We calculate chemical products of the fireball by dividing the shocked air into concentric shells. Each shell is shocked to a peak temperature T'. The mass of a shell is determined from Eq. 1. The final chemical products are summed over all shells. Chemical products for wet and dry air are listed in Table 1 for a 10^{14} g impactor; the numbers given in the Table are based on the upper bound from Eq. 1. If the lower bound is adopted yields drop by a factor of ten.

Eqs. 2 and 3 determine the mass of air shocked to temperatures greater than T' in the reentry shock. Each annulus cools from T' as described by Eq. 4. A constant pressure of 1 mbar was assumed unless otherwise noted; results differ somewhat for other pressures. Final chemical products for a 10^{14} g impactor are listed in Table 2. Essentially all the S_8 in Table 2 was at one time S_2. Evidently the HST first observed S_2 before it converted to S_8.

Table 1. Sulfur Products from the Fireball (g)[a]

species	WC[b]	DC[c]	DA[d]	WA[e]
H_2S[f]	—	3(11)	>4(13)	>4(13)
S_2	2(5)	2(12)	7(12)	6(12)
CS	—	2(5)	1(13)	4(4)
CS_2	—	2(12)	8(11)	3(8)
OCS	—	1(12)	—	1(11)
SO	5(8)	2(5)	—	1(10)
SO_2	5(12)	3(4)	—	2(10)
CO	5(13)	7(13)	—	8(13)
H_2O[f]	4(13)	1(9)	—	>3(14)

[a] Assumes a 10^{14} g comet. 3(11) = 3 x 10^{11}

[b] Wet Comet; solar C:N:S:H_2O.

[c] Dry Comet; solar C:N:S; H_2O is 30% solar.

[d] Dry Air; C:N:S enhanced by 2.3:1.5:7 over solar.

[e] Wet Air; assumes solar C/O.

[f] Present in unprocessed air; lower limits only.

The Comet

The comet provides a second chemical environment, one that is unlike jovian air. We consider two "comet" compositions: a "wet" comet with a solar water to carbon ratio, and a "dry" comet from which 70% of the water has been lost. By construction the comets contain only the hydrogen in water and organic matter, the latter with an assumed C/H ratio of one. Cometary products of the fireball and the reentry shock are listed in Tables 1 and 2.

The reported detection of a great deal of hot water [*Bjoraker pers. comm.* 1994] in the minutes immediately following the impact argues that the comet was water-rich (C/O< 1). According to Table 2 the major sulfur species produced from such a comet would be SO_2,which, as noted earlier, was not detected by HST. On the other hand, the reported detection of a great deal of OCS [*Lellouche et al.*, 1995] argues that the comet was dry. Here rmains a puzzle.

Thermochemical Equilibrium

Thermochemical equilibrium calculations in solar, dry solar, and cometary gas provide a complementary perspective. We use the CONDOR code and database described by *Fegley and Lodders* [1994a]. Approximately 2000 gases of all naturally occurring elements in the periodic table were included in these calculations [*Fegley and Lodders,* 1994b].

At high temperatures (>3500 K, essentially independent of total pressure), ionized and atomic sulfur are the dominant species. With cooling of the fireball, the radicals HS and CS become important, their abundances eventually drop with continued cooling and H_2S, S_2, and CS_2 become important at low temperatures. Figure 3 illustrates that the abundances of S_2 and CS_2 are sensitive to temperature and pressure, and both peak at low temperatures ($\approx$1000 K) and low pressures (1 μbar and below). The CS radical constitutes a significant fraction of total sulfur over wide T and P ranges, but is probably unquenchable save at very low pressure. The plausible major sulfur species resulting from shock induced chemical reprocessing of jovian gas are H_2S, S_2, CS_2 and at low pressures, CS.

Thermochemical equilibrium calculations show that H_2S and S_2 also result from shock heating of solar gas, i.e. wet jovian air. But production of CS and CS_2 is suppressed. In their place we find oxides such as SO, SO_2, and OCS. Shock heating of cometary gas, using compositions for P/Halley given by *Anders and Grevesse* [1989], also yields H_2S and S_2, but again large amounts of SO_2, SO, and other oxidized sulfur species also form.

Although these preliminary results of the thermochemical equilibrium calculations differ in detail from those of the kinetic model, both sets of calculations show the same major conclusions, namely that S_2 and CS_2 production is a natural consequence of shock heating and quenching dry jovian gas. Both sets of calculations also show that shock heating of wet jovian gas and of cometary gas leads to the production of oxidized sulfur gases, exemplified by SO_2 and SO.

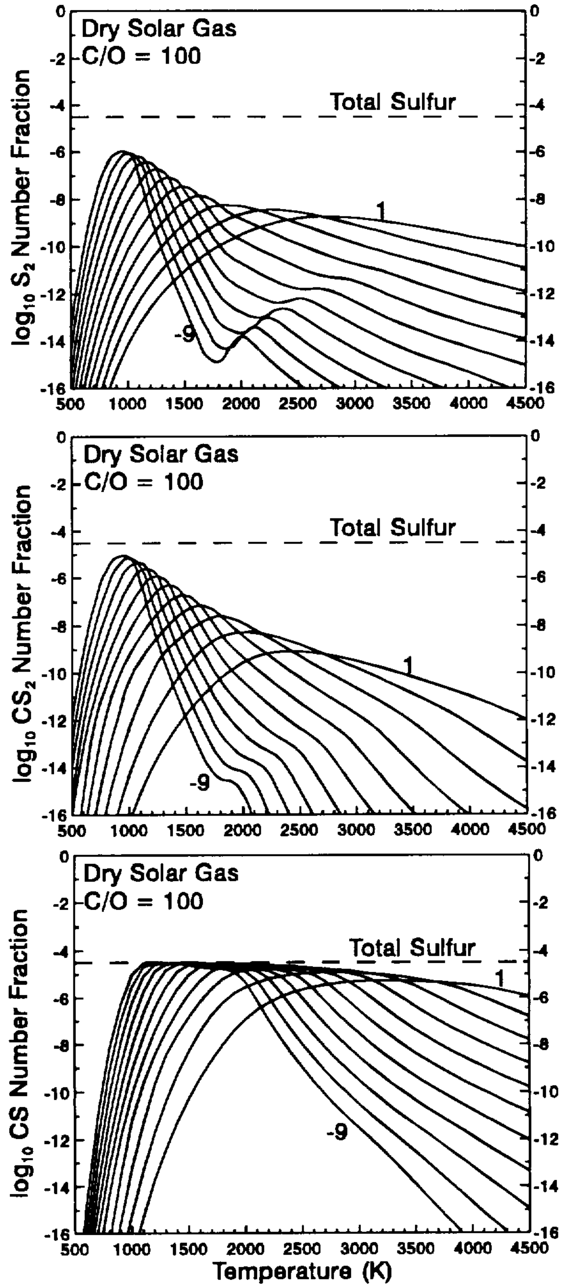

Figure 3. Thermochemical equilibria of S_2, CS_2, and CS as functions of temperature and pressure in dry solar gas with a C/O atomic ratio of 100. This ratio is equivalent to the CH_4/H_2O ratio at 200 K, in the NH_4SH cloud layer on Jupiter. Isobars from 1 to 10^{-9} bars and temperatures from 500 K to 4500 K are considered. Higher temperatures lead to increasing amounts of atomic and ionized sulfur and are not graphed.

Table 2. Sulfur Products from the Reentry Shock (g)^g

species	WC^b	DC^c	DA^d	DA^{dh}	WA^e
H_2S^{f}	5(6)	7(10)	>1(13)	>1(13)	>4(12)
S_2	2(5)	1(9)	3(9)	5(8)	2(10)
S_8	—	2(12)	6(12)	4(12)	9(12)
CS	—	—	—	7(12)	—
CS_2	—	2(12)	4(10)	3(11)	4(8)
OCS	7(7)	4(11)	—	—	5(9)
SO	3(8)	—	—	—	1(11)
SO_2	5(12)	—	—	—	1(12)
CO	5(13)	7(13)	—	—	5(13)
H_2O^{f}	4(13)	1(7)	—	—	>9(13)

[g] Assumes a 10^{14} g comet and p' = 1 mbar.
[h] p' = 0.1 mbar.

Summary

Diatomic sulfur was a major unexpected product of adding P/Shoemaker-Levy 9 to Jupiter. The S_2 and CS_2 were apparently concentrated at high altitudes, the latter above a millibar [*Yelle and McGrath, pers. comm.*, 1995], which is consistent with the sulfur falling from above; i.e., S_2 and CS_2 were produced where the hypersonic ejecta plume fell back on the atmosphere. A sulfur content of 0.3% sulfur by mass [*de Pater,* 1991] would place the reported column [*Noll et al.*, 1995] of S_2 above 400 μbars. Kinetic and thermochemical equilibrium models presented here show that the low pressure and extreme disequilibrium chemistry of the reentry shock strongly favor the generation of S_2. Eventually S_2 converts to S_8 when the gas cools. Survival of S_2 is favored by low pressure and high temperature. *Moses et al.* [1995] show that conversion to S_8 is slow above 100 μbars, where low density and photolysis prevent polymerization.

Shocks in dry jovian air produce mostly S_2, H_2S, CS_2, and at low pressures, CS. These were the observed species, and the calculated S_2/CS_2 ratio is in reasonable agreement with that observed. Shocks in wet jovian air also produce abundant S_2, but the oxides SO_2 and SO replace CS and CS_2 as important other species. Oxides were not observed by the HST [*Noll et al.*, 1995]. Apparently the comet did not excavate much air from below the jovian water table.

Shocks in the comet itself produce SO_2 if the comet is wet, and CS_2, S_2, and OCS if the comet is dry. The detection of hot water implies that the comet was wet, but the detection of OCS implies that the comet was dry. Any comet produces CO. The apparent absence of SO_2 might be explained by spreading the ex-comet over the full breadth of the ejecta blanket. An alternative explanation is that the comet, being relatively dense, is mostly buried beneath the center of the explosion [*Crawford et al.*, 1994]. The latter possibility is consistent with small amounts of SO_2 but inconsistent with large amounts of water, CO, and OCS.

The calculated mass of S_2 produced by a 10^{14} g impact falls about an order of magnitude short of the reported 5×10^{13} g [*Noll et al.*, 1995]. A 10^{15} g impactor is needed to produce this much S_2. Either Jupiter is considerably more rich in sulfur than we have assumed; the observed amount of S_2 has been overestimated; photolysis by UV radiation from the fireball was much more effective than shocks at driving chemistry; or the impactors were larger than the 10^{14} g fragments deduced by *Asphaug and Benz* [1994] from the gravitational dynamics of tidal disruption and re-accretion and by *Zahnle and Mac Low* [1995] from the infrared luminosity of the R fragment plumefall.

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