

HOT-ATOM SYNTHESIS OF ORGANIC COMPOUNDS ON JUPITER

JOHN S. LEWIS AND BRUCE FEGLEY, JR.

Department of Earth and Planetary Sciences, Massachusetts Institute of Technology

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ABSTRACT

Results of recent laboratory "simulations" of photochemical processes on Jupiter are combined with available data on mixing rates and exposure times in the Jovian atmosphere to give quantitative predictions of the rate at which hot-atom reactions produce organic molecules. It is shown that abstraction reactions on methane by hot H atoms from solar UV photolysis of H₂S will produce no more than 4×10^{-17} g cm⁻² s⁻¹ for a steady-state mole fraction of total organics of $\sim 10^{-16}$. This is roughly 10⁷ times less than the limit of detection of the most sensitive gas analysis experiments ever flown on a spacecraft. By far the most common organic molecule produced by this mechanism is CH₃SH, methyl mercaptan, which is produced at a rate at least 600 times smaller than the rate of production of ethane by direct photolysis of CH₄ at high altitudes.

Subject headings: molecular processes — planets: atmospheres — planets: Jupiter

Recent experimental "simulations" of the photolysis of H₂S containing mixtures in the atmosphere of Jupiter have provided information on the product yields and identities for a number of complex organic species under the conditions of the simulation (Sagan and Khare 1971*a,b*; Khare and Sagan 1971, 1973; Khare *et al.* 1978). It is our purpose in this *Letter* to combine information on the nature of hot-atom reactions, on mixing times in the Jovian atmosphere, and on the production rates and steady-state abundances of organic matter formed on Jupiter in order to assess this mechanism quantitatively. We are able to show that hot-atom reactions are a negligible source of organic matter on Jupiter, due in part to the low UV flux at Jupiter, in part to rapid vertical mixing of the atmosphere, and in part to efficient thermalization of hot H atoms in Jupiter's atmosphere.

First, we have the conditions of the "simulation": roughly equimolar amounts of CH₄, NH₃, H₂S, and C₂H₆ and some water vapor were irradiated for a total exposure time of 418.6 hours with a near-UV source giving 5.8 W at the mercury 2537 Å line (Khare *et al.* 1978). Hot atomic hydrogen is produced by photolysis of H₂S, the only gas present which predissociates at this wavelength. This atomic hydrogen is produced on Jupiter by photons of $\lambda > 2350$ Å (5.3 eV) (Gann and Dubrin 1967), shortward of which ammonia gas shields H₂S, but of $\lambda < 2700$ Å (4.6 eV), beyond which H₂S does not dissociate. The dissociation energy of the H—SH bond is 3.9 eV—leaving the fragments with kinetic energies of 0.7 to 1.4 eV—almost all of which is carried by the H atom, which has an energy close to 2000 K. This atom can abstract H from CH₄, NH₃, or C₂H₆, giving highly reactive free radicals which combine to form complex H, C, N, O, S compounds. Near-total destruction of the available H₂S occurs, giving ~ 7 g of products. On a sulfur-free basis the "organic" content of the products (H, C, N, O compounds) is 5% by weight, or 0.35 g. The total

energy input from the lamp is 8×10^{13} ergs, for an efficiency of production of organic matter of 4×10^{-15} g erg⁻¹. The production of organic matter is, of course, greatly enhanced by the conditions of the experiments, since on Jupiter the overwhelming predominance of H₂ and He will lead to rapid thermalization of hot H atoms by collision, thus rendering them vastly less effective at abstracting H atoms.

In order to scale the results of these laboratory experiments to Jupiter, we need to know both the magnitude of the solar UV flux which goes into dissociating H₂S, and the time scale for atmospheric overturn at the level where H₂S photolysis occurs. We must also scale the production of organic matter to allow for the more efficient thermalization of hot H atoms on Jupiter relative to the laboratory experiment. Fortunately, all the data needed to make these corrections are available.

First, we scale for exposure time. On Jupiter, the Sun provides ~ 60 ergs cm⁻² s⁻¹ for H₂S photolysis (Prinn 1970; Lewis and Prinn 1970). Stone (1976) has shown that the observed heat flux from the interior of Jupiter, $\sim 10^4$ ergs cm⁻² s⁻¹, must be carried by strong turbulent convection. The atmospheric overturn is modeled as a one-dimensional random walk (eddy diffusion), which is described by a constant K (cm² s⁻¹) analogous to a diffusion constant. Stone showed that the value of K needed to transport the absorbed heat flux out of Jupiter's interior by free convection is between 10^7 and 10^9 cm² s⁻¹ at levels in the atmosphere where the pressure is a few bars. Clearly, strong vertical mixing can transport upward species which are stable at high pressures and temperatures, but unstable near the observed level. Three such tracers of deep atmospheric motions are known. Ridgway (1974) has reported the presence of PH₃, interpreted by Prinn and Lewis (1975) as a tracer of deep mixing. Carbon monoxide, observed by Beer (1975), has been shown by Prinn and Barshay (1977) to be plausibly explained

1979ApJ...232L..135L

by rapid vertical transport from levels where the temperature is ~ 1000 K up to the ~ 300 K level. Fink, Larson, and Treffers (1978) have also presented evidence for the presence of another tracer, germane, GeH_4 , a species expected on theoretical grounds to be yet another likely tracer of deep mixing (Barshay and Lewis 1978). Prinn and Barshay's work on CO shows that the rates of the known reactions destroying CO require overturn at a rate corresponding to $K = 2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$, with an uncertainty of about a factor of 10. The time scale for mixing out of the region of photolysis to a depth of one scale height H is just H^2/K , or $\sim 3 \times 10^4$ s. Thus any parcel of atmosphere will encounter a total of $\sim 1.8 \times 10^6 \text{ ergs cm}^{-2}$ UV during its exposure time. (Note that the experiment involved $8 \times 10^{13} \text{ ergs}$ in a few cm^2 , corresponding to $\sim 10^7$ times the total exposure a gas parcel on Jupiter could experience. A better simulation of irradiation experienced on Jupiter would have been achieved if the light source had been run for $418.6 \text{ hr} \times 10^{-7}$, or 0.15 s.) Using the observed efficiency of production of organic matter in the "simulation," the Jovian gas should contain after exposure $7 \times 10^{-9} \text{ g cm}^{-2}$ of H, C, N, O compounds on a sulfur-free basis, before scaling for the thermalization of hot H atoms. This is a production rate of $\sim 2 \times 10^{-13} \text{ g cm}^{-2} \text{ s}^{-1}$.

Next, we scale for thermalization of hot H atoms on Jupiter. The probability of a hot-atom collision with a methane molecule in any given collision is proportional to the product of the mole fraction f_{CH_4} , times the square of the molecular diameter, $d_{\text{CH}_4}^2$. This normalized probability, calculated for solar elemental abundances of H, He, and C, is 5×10^{-4} . The probability that the H- CH_4 collision will be reactive lies in the range 10^{-3} to 10^{-1} (Thrush 1965; Steacie 1954); Martin and Willard (1964) found a value of 3.1×10^{-3} . We shall use a generous upper limit for the reactive probability of 10^{-2} . Then abstraction reactions from methane on Jupiter shall result from *at most* 5×10^{-6} of the collisions involving hot H atoms. The fate of the 86% of the hot H atoms which strike an H_2 molecule first is to suffer a major loss of energy. The mean speed of H in the laboratory system after scattering is two-thirds times the speed prior to the collision, for a kinetic energy loss of 56% per collision. After two collisions, the hot atom will be thermalized to only 19.5% of its original energy (equivalent to 390 K).

In the laboratory "simulation" hot H atom collisions

with molecules as heavy as CH_4 , NH_3 , H_2O , etc. (say, molecular weight 17), the energy after collision is on the average $(16/17)^2 = 0.88$ times the incident energy. Thermalization to below 400 K then requires $n = \log(400/2000)/\log(0.88)$ or 13 collisions. If the probability of an H atom reacting during a collision with a heavy molecule is taken to be the very highest allowable (0.01), then the probability of a hot-atom reaction with CH_4 or NH_3 on Jupiter is $[1 - (0.99)^{13}] 5 \times 10^{-4}$, while in the laboratory "simulation" it is $1 - (0.99)^{13}$. Thus the laboratory yields must be scaled by the ratio of these quantities, or 6×10^{-5} . Since 0.35 g of sulfur-free organic material is made per 7 g of sulfur in the "simulation," scaling to Jupiter would give a predicted yield of $2 \times 10^{-5} \text{ g}$ of organic matter per 7 g of sulfur, for a weight fraction of 3×10^{-6} .

The steady-state abundance of such organic compounds on Jupiter is then $4 \times 10^{-13} \text{ g cm}^{-2}$. The mass of atmosphere into which this organic matter is mixed is *at least* that above the $\sim 2b$ level where H_2S photolyses, 800 g cm^{-2} , for a mass fraction of organic material of $< 5 \times 10^{-16}$. This corresponds to a maximum mole fraction of $f_{\text{org}} = 5 \times 10^{-17}$ for C_2 hydrocarbons, and less if the organic molecules formed are more complex. This is about 10^7 times smaller than the detection limit of the most sensitive gas analysis instrument ever flown on a planetary probe, the *Viking* GC/MS.

The overall efficiencies for production of sulfur are remarkably similar in the laboratory and on Jupiter, considering the many differences in conditions: $\sim 8 \times 10^{-13} \text{ g sulfur erg}^{-1}$ on Jupiter, and $\sim 10^{-13} \text{ g sulfur erg}^{-1}$ in the laboratory. Thus effects such as artificial enhancement of the laboratory yield due to nonlinearity of polymerization rates with UV flux are unimportant.

We should also briefly mention the fate of thermalized H atoms. It is relatively simple to compute the photochemical steady-state abundances of H, SH, and CH_3 due to H_2S photolysis, and to estimate production rates of organic species from reactions of the thermalized H atoms. We consider $\text{H} + \text{H} + \text{M}$, $\text{H} + \text{SH} + \text{M}$, and $\text{H} + \text{H}_2\text{S}$ as possible loss reactions for H. Of these, the latter is by far the fastest, giving a steady-state H concentration of $n_{\text{H}} \approx 4 \times 10^2 \text{ cm}^{-3}$. We consider $\text{SH} + \text{H} + \text{M}$, $\text{SH} + \text{CH}_3 + \text{M}$, $\text{SH} + \text{SH} + \text{M}$, and $\text{SH} + \text{SH}$ as possible loss routes for SH, with the rate constants given in Table 1. The peak photolysis rate for H_2S is $10^6 \text{ cm}^{-3} \text{ s}^{-1}$ near the 220 K level. We

TABLE 1
KINETIC DATA

Reaction	Rate Constant at 220 K	Source
1. $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$3 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$	Kondratiev
2. $\text{H} + \text{SH} + \text{M} \rightarrow \text{H}_2\text{S} + \text{M}$	$1.3 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$	Estimated from $\text{H} + \text{OH} + \text{M}$
3. $\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{SH}$	$2.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Baulch <i>et al.</i>
4. $\text{SH} + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{SH} + \text{M}$	$1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$	Estimated
5. $\text{SH} + \text{SH} \rightarrow \text{H}_2\text{S}_2$	$1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	Baulch <i>et al.</i>
6. $\text{SH} + \text{SH} + \text{M} \rightarrow \text{H}_2\text{S}_2 + \text{M}$	$1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$	Estimated
7. $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$	$6 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$	Kondratiev

then find that the latter two reactions are dominant, with the three-body mechanism several times as fast as the two-body reaction. A steady-state SH abundance of $\sim 10^8 \text{ cm}^{-3}$ follows. The rate of thermal abstraction of H atoms from CH_4 at the 220 K level is then only $3.2 \times 10^{-4} \text{ cm}^{-3} \text{ s}^{-1}$, for a total yield of CH_3 radicals of $\sim 10 \text{ cm}^{-3}$ over the mixing time. Thus no organic species can possibly be made with a mole fraction greater than $\sim 10^{-19}$.

Therefore thermalized H atoms have negligible effect in organic synthesis even compared with hot-atom synthesis. Clearly, recombination with abundant SH is the most likely fate of CH_3 , and the dominant organic molecule must be CH_3SH . Barshay and Lewis (1978) have, however, shown that thermal equilibrium deep within the Jovian atmosphere produces a CH_3SH mole fraction $\geq 4 \times 10^{-16}$ any temperature above 500 K. Indeed, quenching by rapid cooling of gas from the $\sim 1000 \text{ K}$ level (where CO , PH_3 , and GeH_4 are stable at their observed abundances) would give a CH_3SH fraction of 2×10^{-12} . Thus even successful detection of CH_3SH on Jupiter could not be taken as evidence for the importance of hot or cold H atom reactions.

The dominance of CH_3SH over all other organic hot-atom products on Jupiter is obvious. The formation of more complex products in the "simulation" is due not only to the very high probability of hot-atom collisions with heavy molecules, but also to the presence of large amounts of ethane: the activation energy for H abstraction reactions from ethane is only 9.7 kcal mole $^{-1}$ compared with 12.7 kcal mole $^{-1}$ for CH_4 (Kondratiev 1972). Thus H abstraction from ethane can greatly augment the complexity of organic matter

in the laboratory, where the C_2H_6 mole fraction is enormously higher than in the Jovian troposphere.

The production rate of C_2 hydrocarbons by direct photolysis of methane at high altitudes is $\sim 2.5 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (Strobel 1973). The convective flux at the 2 bar, 220 K level is $\rho v_s \approx \rho K/H = 7 \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1}$, for an ethane mole fraction at that level of only $\sim 7 \times 10^{-14}$. This compares with an ethane mole fraction $> 10^{-1}$ in the laboratory "simulation." The production rate of organics (i.e., CH_3SH) by hot-atom reactions is 600 times smaller than the feeble direct production of C_2H_6 by CH_4 photolysis. It is also $\sim 10^5$ times smaller than the production rate of red phosphorus (Prinn and Lewis 1975) and nearly 10^6 times smaller than that of yellow, orange, and brown sulfur species (Lewis and Prinn 1970). The latter is, of course, a necessary logical precondition for the existence of the hot-atom mechanism proposed by Sagan and Khare (1971*a,b*).

These conclusions regarding relative production rates are insensitive to the details of the Jupiter model employed. The absolute steady-state concentrations of products scale inversely with the eddy diffusion coefficient, K , and will vary regionally in a complex manner. Their global average values may differ from those estimated herein by a factor of 10. Such uncertainties are several orders of magnitude too small to cast doubt on the qualitative conclusion that hot-atom production of organic matter on the Jovian planets is of negligible importance.

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REFERENCES

- Barshay, S. S., and Lewis, J. S. 1978, *Icarus*, **33**, 593.
 Baulch, D. L., Drysdale, D. D., Duxbury J., and Grant, S. 1976, *Evaluated Kinetic Data for High Temperature Reactions* (Boston: Butterworths), Vol. 3.
 Beer, R. 1975, *Ap. J. (Letters)*, **200**, L111.
 Fink, U., Larson, H. P., and Treffers, R. R. 1978, *Icarus*, **34**, 344.
 Gann, R. G., and Dubrin, J. 1967, *J. Chem. Phys.*, **47**, 1867.
 Khare, B. N., and Sagan, C. 1971, *Nature*, **232**, 577.
 ———. 1973, *Icarus*, **20**, 311.
 Khare, B. N., Sagan, C., Bandurski, E. L., and Nagy, B. 1978, *Science*, **199**, 1199.
 Kondratiev, V. N. 1972, *Rate Constants of Gas Phase Reactions* (NBS).
 Lewis, J. S., and Prinn, R. G. 1970, *Science*, **169**, 472.
 Martin, R. W., and Willard, J. E. 1964, *J. Chem. Phys.*, **40**, 3007.
 Prinn, R. G. 1970, *Icarus*, **13**, 424.
 Prinn, R. G., and Barshay, S. S. 1977, *Science*, **198**, 1031.
 Prinn, R. G., and Lewis, J. S. 1975, *Science*, **190**, 294.
 Ridgway, S. T. 1974, *Bull. AAS*, **6**, 376.
 Sagan, C., and Khare, B. N. 1971*a*, *Ap. J.*, **168**, 563.
 ———. 1971*b*, *Science*, **173**, 417.
 Steacie, E. W. R. 1954, *Atomic and Free Radical Reactions* (New York: Reinhold), p. 496.
 Stone, P. 1976, in *Jupiter*, ed. T. Gehrels (Tucson: University of Arizona Press), p. 586.
 Strobel, D. 1969, *J. Atmos. Sci.*, **26**, 906.
 ———. 1973, *J. Atmos. Sci.*, **30**, 489.
 Thrush, B. A. 1965, *Prog. Reaction Kinetics*, **3**, 63.

BRUCE FEGLEY, JR., and JOHN S. LEWIS: Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

1979ApJ...232L135L