

Benzene and Haze Formation in the Polar Atmosphere of Jupiter

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[1] Jupiter has a large magnetosphere that episodically precipitates large amounts of energy into the polar atmosphere, giving rise to intense auroras [Clarke *et al.*, 1996; Grodent *et al.*, 2000]. An important consequence of this energy influx is the production of a dark haze [Pryor and Hord, 1991], the formation mechanism of which was hitherto poorly known. Recent observations of benzene on Jupiter [Bézard *et al.*, 2001; Flasar, 2002] provide new clues for a chemical and aerosol model for the formation of heavy hydrocarbon aerosols. The chemistry begins with the destruction of methane by energetic particles, followed by neutral and ion reactions, ultimately leading to the formation of benzene and other complex hydrocarbons, including multi-ring compounds which subsequently condense. High temperatures and effective eddy mixing engendered by the auroras enhance the formation of heavy hydrocarbons and aerosols. This mechanism may be relevant in the atmospheres of Saturn and extrasolar giant planets, and is an example of how a planetary magnetosphere may influence the chemical composition and climate forcing of the upper atmosphere. **INDEX TERMS:** 5704 Planetology: Fluid Planets: Atmospheres—composition and chemistry; 6220 Planetology: Solar System Objects: Jupiter; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 2407 Ionosphere: Auroral ionosphere (2704); 2419 Ionosphere: Ion chemistry and composition (0335). **Citation:** Wong, A.-S., Y. L. Yung, and A. J. Friedson, Benzene and Haze Formation in the Polar Atmosphere of Jupiter, *Geophys. Res. Lett.*, 30(8), 1447, doi:10.1029/2002GL016661, 2003.

1. Benzene Observations

[2] Benzene was first detected on Jupiter in 1985 by the Voyager Infrared Interferometer Spectrometer (IRIS) experiment in the northern auroral region near 60°N and 180°W [Kim *et al.*, 1985]. Observations with the Short-Wavelength Spectrometer (SWS) of the Infrared Space Observatory (ISO) indicate the presence of benzene at all latitudes, with emission enhancement of the ν_4 band in the auroral regions [Bézard *et al.*, 2001]. The inferred abundance is $9(+4.5, -7.5) \times 10^{14}$ molecules cm^{-2} above the 50-mbar altitude level in mid-latitude non-auroral regions. Recently, the Composite Infrared Spectrometer (CIRS) aboard the Cassini

spacecraft, during Jupiter swingby, has also observed benzene at northern and southern high latitudes, with significantly enhanced emission in the auroral spots relative to the surrounding regions [Flasar, 2002].

2. Model Description and Results

[3] In the polar regions, since there is insufficient UV flux to produce the observed amount of benzene, energy from the auroras might be necessary. To investigate the effects of the auroras on benzene and aerosol production in polar regions, a new Caltech/JPL one-dimensional chemical model of hydrocarbons for Jupiter is presented here, with updated neutral and ion kinetics and aerosol modeling [Gladstone *et al.*, 1996; Moses *et al.*, 2000; Lee *et al.*, 2000; Wong *et al.*, 2000; Friedson *et al.*, 2002]. The calculations are made for 60° latitude. Chemical species calculated include linear and/or cyclic hydrocarbon neutral molecules and ions up to six carbon atoms (including the ring compound benzene A_1 and its radical A_1^-), the two-ring compound naphthalene (A_2) and its radicals, one- and two-ring compounds with one or two hydrogen atoms replaced by C_2H_2 group, and polycyclic aromatic hydrocarbons (PAHs) larger than A_2 lumped together as one species. Long chain hydrocarbons will be addressed in a separate study. The complete list of reactions and rate coefficients is tabulated in Appendix B.1.4 of Wong's thesis [Wong, 2002]. A sample of important reactions is listed in Table 1, and the reaction pathways are illustrated in Figure 1.

2.1. Auroral Atmosphere

[4] In our model, the temperature profiles and auroral ion production rates are taken from the self-consistent Jovian auroral thermal model of Grodent *et al.* [2000] to simulate the diffuse and discrete auroras. In the cool diffuse aurora, the energy flux is $30.5 \text{ ergs cm}^{-2} \text{ s}^{-1}$ whereas in the warm discrete aurora it is $110.5 \text{ ergs cm}^{-2} \text{ s}^{-1}$. The eddy diffusivity profile, $K(z)$, in the auroral regions of Jupiter is not known; however, due to the intense energy input, eddy mixing is expected to be much more effective. For example, on Earth, $K(z)$ in the polar regions is 10–30 times greater than that in the lower latitudes [Banks and Krocharts, 1973]. By analogy, we surmise that in Jupiter's auroral regions, at the altitudes of electron deposition, $K(z)$ would be at least 15 times greater than that derived by Atreya *et al.* [1981] for the equatorial regions. In our model, we adopt the expression $K(z) = (1.46 \times 10^6 \times 15) \times (1.4 \times 10^{13}/n_e(z))^{0.65} \text{ cm}^2 \text{ s}^{-1}$

Table 1. Selected Reactions and Rate Coefficients for Jupiter Auroral Model

No.	Reaction	Rate Coefficient ^a
R104	$C_3H_2 + H + M \rightarrow C_3H_3 + M$	$k_0 = 2.52 \times 10^{-28}$ $k_\infty = 5.0 \times 10^{-11}$
R123	$C_4H_2 + H + M \rightarrow C_4H_3 + M$	$k_0 = 1.0 \times 10^{-28}$ $k_\infty = 1.39 \times 10^{-10}$ $e^{-1184/T}$
R200	$C_3H_3 + C_3H_3 + M \rightarrow C_6H_6 + M$	$k_0 = 6.0 \times 10^{-28}$ $e^{1680/T}$ $k_\infty = 1.2 \times 10^{-10}$
R203	$C_4H + H_2 \rightarrow C_4H_2 + H$	$1.2 \times 10^{-11} e^{-998/T}$
R233	$C_3H_3 + C_3H_3 \rightarrow A_1 + H$	4.98×10^{-12}
R234	$C_3H_3 + C_3H_2 + M \rightarrow A_1 + M$	4.98×10^{-12}
R242	$C_4H_3 + C_2H_2 + M \rightarrow A_1 + M$	$4.65 \times 10^{-21} T^{-2.9}$ $e^{-703.59/T}$
R244	$C_4H_5 + C_2H_2 \rightarrow A_1 + H$	$1.66 \times 10^{-08} T^{-1.33}$ $e^{-2714.54/T}$
R255	$C_6H_4 + H + M \rightarrow A_1 + M$	$k_0 = 1.0 \times 10^{-27}$ $k_\infty = 6.33 \times 10^{-13}$
R260	$C_6H_6 + H \rightarrow A_1 + H$	$1.44 \times 10^{-7} T^{-1.3}$ $e^{-1762/T}$
R484	$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2$	2.16×10^{-10}
R546	$C_3H_5^+ + C \rightarrow C_4H_3^+ + H_2$	1.0×10^{-9}
R547	$C_3H_5^+ + C_2H_2 \rightarrow C_5H_5^+ + H_2$	3.8×10^{-10}
R548	$C_3H_5^+ + C_3H_4 \rightarrow c-C_6H_7^+ + H_2$	3.8×10^{-10}
R565	$C_4H_3^+ + C_2H_2 \rightarrow c-C_6H_5^+$	2.2×10^{-10}
R589	$c-C_6H_5^+ + H_2 \rightarrow c-C_6H_7^+$	6.0×10^{-11}
R640	$C_3H_5^+ + e^- \rightarrow C_3H_3 + H_2$	$2.6 \times 10^{-6} T^{-0.5}$
R646	$C_4H_3^+ + e^- \rightarrow C_4H_2 + H$	$5.37 \times 10^{-6} T^{-0.5}$
R667	$c-C_6H_7^+ + e^- \rightarrow A_1 + H$	$8.66 \times 10^{-6} T^{-0.5}$

The full reaction list and the references are available from the authors²³.

^aUnits for two-body (k_∞) and three-body (k_0) rate coefficients are $cm^3 s^{-1}$ and $cm^6 s^{-1}$, respectively.

above 100 mbar, and $K(z) = 10^3 cm^2 s^{-1}$ below 100 mbar, where $n_i(z)$ is the total number density as a function of altitude z .

2.2. Photochemistry and Ion Chemistry

[5] For neutral chemistry, there is little consensus regarding the dominant reactions responsible for the first aromatic ring formation [see, e.g., Lindstedt, 1998]. Among the more widely accepted processes, the two most important pathways are 1) the combination of propargyl radicals C_3H_3 , and 2) C_2H_2 addition to $n-C_4H_3$ (HCCCHCH) or $n-C_4H_5$ (CH₂CHCHCH). We adopt the rate coefficients for these two pathways from the evaluation by D'Anna et al. [2001].

[6] For ion chemistry, we select relevant ion reactions from over 4000 reactions in the literature [Perry et al., 1999; Anicich and McEwan, 1997; Keller et al., 1998; Kim and Fox, 1994; Le Teuff and Markwich, 2000; McEwan et al., 1999; Millar et al., 1997; Scott et al., 1997; Vinckier et al., 1962]. Ion chemistry starts with the most important electron-impact reactions which ionize H_2 , H, and He; the production rates are taken from Grodent et al. [2000] for both diffuse and discrete aurora cases. Eight photoionization reactions are included for comparison with the electron-impact ionization and are found to be negligible at this latitude. The ions react with and transfer charges to neutral species through ion-neutral exchange reactions, and 288 exchange reactions are included in the calculation. The ions also recombine with electrons to form neutral species. Our model includes 79 electron-ion recombination reactions.

[7] Several outstanding uncertainties exist in selecting ion reactions for the model. First, for most reactions that

form $C_6H_5^+$ or $C_6H_7^+$ it is not known whether the products are in cyclic form or not, because most of the experimental data are based on mass spectrometry. We assume the cyclic forms for these species because ring closure will occur when radiative stabilization dominates [McEwan et al., 1999]. Second, the rate coefficients and/or branching ratios of some ion reactions are unavailable. For these reactions, we estimate the total rate coefficient to be $10^{-9} cm^3 s^{-1}$, and assume equal branching ratios for all branches when applicable. Three-body reaction rate coefficients are not available for most ion-neutral exchange reactions, and we assign an estimated rate coefficient of $1.0 \times 10^{-27} cm^6 s^{-1}$. Finally, for those electron-ion recombination reactions with unavailable product and rate information, we estimate a removal rate coefficient of $7.5 \times 10^{-7} cm^3 s^{-1}$ [Perry et al., 1999; Rebrion-Rowe et al., 1998], and we use C_iH_n to represent the sum of species formed from the electron recombination of an ion which has a total of i carbon atoms. These C_iH_n molecules are removed in the model only by eddy diffusion. Hydrocarbon molecules larger than benzene do not react with ions in the model.

2.3. Chemical Model Results

[8] For a diffuse aurora with $30.5 ergs cm^{-2} s^{-1}$ input energy flux; the calculated column abundance of benzene above the 50-mbar pressure level is 4.3×10^{15} molecules cm^{-2} , the mixing ratio at 10^{-3} mbar is 2.6×10^{-8} , and the total production rate is 2.5×10^8 molecules $cm^{-2} s^{-1}$. The calculated volume mixing ratios of the relevant species are shown in Figure 2a. For a discrete aurora with $110.5 ergs cm^{-2} s^{-1}$ input energy flux for a period of 10^6 seconds, the corresponding values for abundance, mixing ratio and production rate of benzene are 7.5×10^{15} molecules cm^{-2} , 8.6×10^{-8} , and 9.4×10^9 molecules $cm^{-2} s^{-1}$, respectively. As expected, the more intense discrete aurora produces greater amount of benzene.

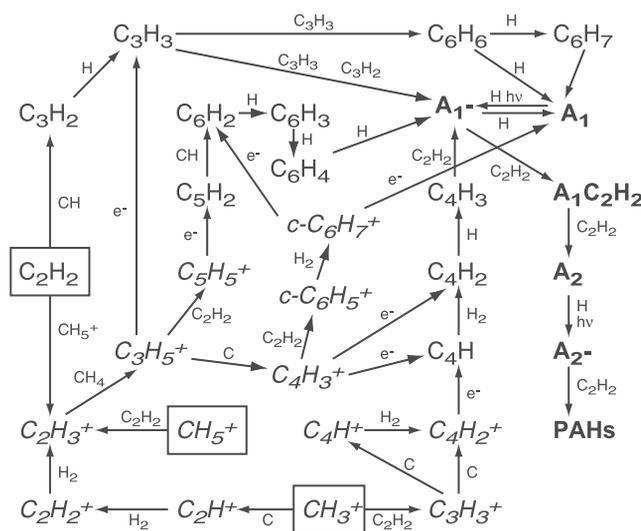


Figure 1. Important reaction pathways of benzene and polycyclic aromatic hydrocarbons formation. A_1 is benzene, A_2 is naphthalene, A_1^- and A_2^- are one and two ring radicals, $A_1C_2H_2$ is benzene with a hydrogen atom replaced by a C_2H_2 group, and PAHs represents all ring compounds larger than A_2 .

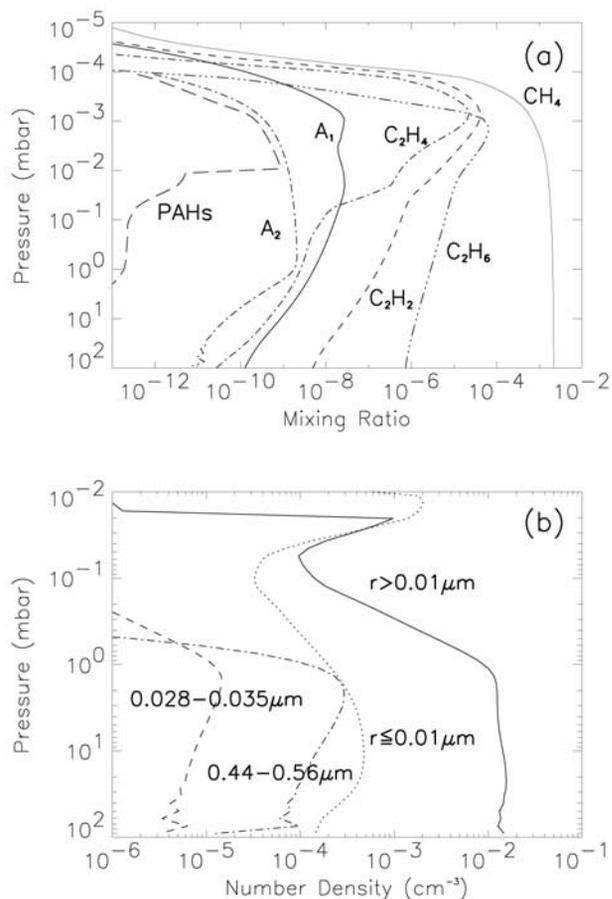


Figure 2. Results of chemical and aerosol model for Jupiter's auroral stratosphere (diffuse aurora), with an electron precipitation energy flux $30.5 \text{ ergs cm}^{-2} \text{ s}^{-1}$. (a) Mixing ratio profiles of CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , benzene (A_1), naphthalene (A_2), and PAHs larger than A_2 . (b) Vertical profiles of aerosol concentration. The particles are assumed to be agglomerates characterized by a fractal dimension of 2.5. Solid line: total concentration of mixed A_2 -PAH particles with volume-equivalent radii $r > 0.01 \mu\text{m}$. Dashed line: concentration of particles with $0.028 \mu\text{m} < r < 0.035 \mu\text{m}$. Dash-dot line: concentration of particles with $0.44 \mu\text{m} < r < 0.56 \mu\text{m}$. Dotted line: concentration of bare PAH nuclei with $r \leq 0.01 \mu\text{m}$.

[9] Our model identifies the important reaction pathways for benzene production, and finds that ion chemistry plays a definitive role. In the case of the diffuse aurora, about 97.6% of the benzene is produced through the electron recombination of ring ion $c\text{-C}_6\text{H}_7^+$, which is formed through successive ion-neutral reactions of ions with C_2H_2 or H_2 , producing C_2H_3^+ , C_4H_3^+ and $c\text{-C}_6\text{H}_5^+$ (Figure 1). The most important neutral pathway, accounting for 2.0% of total benzene production, is the cyclization of C_6H_4 which forms phenyl radical. This pathway is minor in neutral chemistry, but becomes prominent in ion chemistry where recombination of large ions with electrons leads to the eventual production of C_6H_4 . The recombination of C_3H_3 accounts for 0.4% of total benzene production; the abundance of C_3H_3 is enhanced by 5 times by ion chemistry through the electron recombination of C_3H_5^+ . A similar neutral pathway

is identified in studies of benzene formation in Titan's atmosphere [Wilson *et al.*, 2003].

[10] Our model also shows an increase of hydrocarbon abundance with increasing auroral activity. For example, the column abundance of ethylene above 50-mbar is $6.7 \times 10^{15} \text{ cm}^{-2}$ in the diffuse aurora, and is $1.8 \times 10^{16} \text{ cm}^{-2}$ in the discrete aurora. The increase in acetylene and ethane is less significant. For comparison, the Cassini CIRS preliminary observational results show enhanced emission from acetylene and ethylene in auroral regions, with less enhancement from ethane [Flasar, 2002]. However, the enhancement in abundance of these species relative to the surrounding non-auroral regions is unknown, because the auroral vertical temperature profile is still uncertain [Flasar, personal communication].

2.4. Aerosol Model

[11] Ion chemistry and benzene production lead to the formation of complex hydrocarbons and PAHs, which condense to form aerosols (Figure 2b). Coupling the chemical model with the aerosol microphysical model of Friedson *et al.* [2002], we find that, in the diffuse aurora case, the total volume of aerosol produced per unit area is $5.5 \times 10^{-6} \text{ cm}^3 \text{ cm}^{-2}$. For comparison, the total aerosol volume deduced from the data of Tomasko *et al.* [1986] (observation at 40°N) and Rages *et al.* [1999] (observation at 60°N) is around $2 \times 10^{-5} - 3 \times 10^{-5} \text{ cm}^3 \text{ cm}^{-2}$. Mean particle radii are in the range of $\sim 0.09 - 1.1 \mu\text{m}$, with the larger particles residing at lower altitudes. The altitude of the haze top and the mean particle sizes predicted by our model are consistent with the observations, while the total aerosol loading is about a factor of four lower than the observational estimates but probably lies within the range of uncertainty associated with these estimate. Previous models neglecting ion chemistry predict too little aerosol by a factor of 100 [Friedson *et al.*, 2002]. With the inclusion of detailed ion chemistry, the dominant path for benzene production in the polar regions, the current model predicts enough aerosol to match the observations.

3. Conclusion

[12] Our new chemical and aerosol model for the auroral atmosphere of Jupiter predicts the amounts of benzene and aerosol that are consistent with observations. The chemical and aerosol formation processes outlined in this paper are probably applicable to Saturn's atmosphere, although the lower magnetospheric energy input on Saturn might affect the chemical rates at which condensable species will form. Our results also suggest that extrasolar giant planets orbiting close to their primary, where they receive high doses of far-UV irradiation, may be blanketed with a similar organic haze. However, great uncertainties remain in our current understanding and therefore laboratory and planetary measurements of the following would permit a more accurate quantification of the polar benzene and haze production: 1) the reaction kinetics of the ring production process, especially in ion-related reaction rate coefficients and products, 2) the energy spectrum and total energy flux of energetic electrons in Jovian auroras, 3) the chemical, physical and optical properties of polar aerosols, and 4) $K(z)$ at the auroral latitudes.

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