Supplementary Information

Details of our hydrodynamic escape model

S1 Basic equations

We have solved the equations of continuity, momentum, and energy for a multi-component gas assuming spherical symmetry,

$$\frac{\partial n_i}{\partial t} + \frac{1}{r^2}\frac{\partial (n_i u_i r^2)}{\partial r} = \omega_i, \tag{1}$$

$$\frac{\partial u_i}{\partial t} + u_i \frac{\partial u_i}{\partial r} = -\frac{1}{\rho_i}\frac{\partial p_i}{\partial r} - \frac{GM}{r^2} + \sum_j (u_j - u_i)\frac{n_j}{m_i}\mu_{ij}k_{ij}, \tag{2}$$

$$\frac{\partial}{\partial t}\left[\rho\left(\frac{1}{2}u^2 + E\right)\right] + \frac{1}{r^2}\frac{\partial}{\partial r}\left\{\left[\left(\frac{1}{2}u^2 + E + \frac{p}{\rho}\right)\rho u\right] r^2\right\} = -\frac{GM}{r^2}\rho u + q, \tag{3}$$

where t is the time, r is the radial distance from the center, n_i, ρ_i, u_i, p_i, and ω_i are the number density, mass density, radial velocity, partial pressure, and production rate of species i respectively, G is the gravitational constant, M is the mass of the planet, ρ, p, and E are the total mass density, total pressure, and total specific internal energy, respectively, u is the mean gas velocity, μ_{ij} is the reduced molecular mass between species i and species j, and k_{ij} is the collision rate that follows

$$k_{ij} = \frac{k_{\mathrm{B}} T}{\mu_{ij} b_{ij}}, \tag{4}$$

where k_{B} is the Boltzmann constant, T is the temperature, and b_{ij} is the binary diffusion coefficient given by

$$b_{ij} = \begin{cases} 1.96 \times 10^{6}\frac{T^{1/2}}{\mu_{ij}^{1/2}} & \text{for neutral-neutral pair} \\ 4.13 \times 10^{-8}\frac{T}{\mu_{ij}^{1/2}\alpha^{1/2}} & \text{for neutral-ion pair} \\ 8.37 \times 10^{-5}\frac{T^{5/2}}{\mu_{ij}^{1/2}} & \text{for ion-ion pair} \end{cases} \tag{5}$$

where α is the polarizability (Banks and Kockarts, 1973; García Muñoz, 2007). Here, b_{ij}, T, μ_{ij} and α are expressed in $\mathrm{cm^{-1}s^{-1}}$, K, g, and $\mathrm{cm^3}$, respectively. The total internal energy is given by

$$\rho E = \frac{1}{n}\left(\sum_i \frac{n_i}{\gamma_i - 1}\right) p, \tag{6}$$

where γ_i is the ratio of specific heat of species i. We assume that γ_i = 5/3, 7/5, 4/3 for monoatomic gases, diatomic gases, and multiatomic gases. The net heating rate is given by

$$q = q_{\mathrm{abs}} - q_{\mathrm{ch}} - q_{\mathrm{rad}}, \tag{7}$$

where q_{abs} is the heating rate by stellar X-ray and UV absorption, q_{ch} is the rate of net chemical energy expense, and q_{rad} is the radiative cooling rate by infrared active species.

S2 Chemical processes

287 chemical reactions are considered for 30 atmospheric components: H_2, CO, CO_2, H_2O, OH, O_2, H, C, O, $O(^1D)$, CH_4, CH, CH_2, CH_3, H^+, H_2^+, H_3^+, C^+, CH^+, CH_2^+, CH_3^+, CH_4^+, CH_5^+, O^+, CO^+, CO_2^+, O_2^+, OH^+, H_2O^+, and H_3O^+ (Table S1).

The photolysis rate $f_{\mathrm{ph},i}$ is given by

$$f_{\mathrm{ph},i} = n_i \int_\lambda \sigma_i(\lambda) I(\lambda) d\lambda, \tag{8}$$

where $\sigma_i(\lambda)$ is the photodissociation/photoionization cross-section at wavelength λ for species i and $I(\lambda)$ is the X-ray and UV photon flux at wavelength λ. The energy consumed per unit time by this photolysis $q_{\mathrm{ph},i}$ is given by

$$q_{\mathrm{ph},i} = f_{\mathrm{ph},i} \frac{hc}{\lambda_{\mathrm{th},i}}, \tag{9}$$

where $\lambda_{\mathrm{th},i}$ is the threshold wavelength for the photolysis of species i, h is the Planck constant, and c is the speed of light in vacuum. We refer to the photodissociation/photoionization cross-sections provided by " PHoto Ionization/Dissociation RATES " (`http://phidrates.space.swri.edu`). Photolysis of CH_2 is not considered due to the lack of the cross-section data.

In addition to photolysis reactions, this study considers bimolecular reactions. The bimolecular reaction rate f_{R} can be written as

$$f_{\mathrm{R}} = k_{\mathrm{R}} n_i n_j, \tag{10}$$

where n_i and n_j represent the number densities of reactants i and j, respectively, and k_{R} is the corresponding reaction rate coefficient. We refer to the reaction rate coefficients provided by "The UMIST Database for Astrochemistry 2012" (`http://udfa.ajmarkwick.net`). We neglect the formation of molecules that have more than one carbon because of low gas densities in the atmospheric region where outflow to space accelerates. The energy consumed per unit time by the bimolecular reaction is given by

$$q_{\mathrm{R}} = -f_{\mathrm{R}} \Delta E_{\mathrm{R}}, \tag{11}$$

where ΔE_R is the heat of reaction, which is positive for endothermic reactions and negative for exothermic reactions. In the evaluation of the heats of the reactions, we make use of the enthalpies of formation listed in Le Teuff et al. (2000). The energy consumption rate q_ch is calculated by summing the consumed energy by each chemical reaction including photolysis.

S3 Radiative processes

To calculate the profiles of heating and photolysis rates in the atmosphere, the radiative transfer of parallel stellar photon beams in a spherically symmetric atmosphere is calculated by applying the method formulated by Tian et al. (2005). We consider the X-ray and UV absorption by H_2, CO, CO_2, H_2O, OH, O_2, H, C, O, CH_4, CH, and CH_3. The stellar beam is assumed to be absorbed by Beer's Law. The energy deposition in a given layer along each path is then multiplied by the area of the ring (Figure 6 in Tian et al., 2005) to obtain the total energy deposited into the shell segment. The heating rate q_abs is given by the total energy absorbed by each shell divided by the volume of the shell. The X-ray and UV spectrum from 0.1 to 280 nm estimated for the young Sun at the age of 100 Myr are adapted (Claire et al., 2012), whose total XUV flux is $0.58\,\mathrm{J\,m^{-2}\,s^{-1}}$ at the orbit of Earth.

We consider radiative cooling by thermal line emissions of CO, CO_2, H_2O, OH, CH_4, CH, CH_3, H_3^+, OH^+, and H_3O^+. The radiative cooling rate due to a transition from an energy level i to another level j of a radiatively active molecular species s is given by

$$q_{\mathrm{rad},s,ij} = n_{s,i} A_{ij} h\nu_{ij} \beta_{ij}, \tag{12}$$

where $n_{s,i}$ is the population density in the level i, A_{ij} is the spontaneous transition probability, $h\nu_{ij}$ is the energy difference between the level i and level j, and β_{ij} is the photon escape probability. The total radiative cooling rate by the species s is calculated by summing the radiative cooling rates by all transitions. The population density $n_{s,i}$ is calculated under the assumption of LTE as

$$n_{s,i} = n_s \frac{g_i}{Z} \exp\left(-\frac{E_i}{k_\mathrm{B} T}\right) \tag{13}$$

where n_s and Z are the total number density and the partition function of species s, and g_i and E_i are the statistical weight and energy of the level i, respectively. Approximating that half of the photons are emitted outward while the other half is emitted downward and then absorbed by dense, lower atmospheric layers, the bulk escape probability is evaluated by

$$\beta_{ij}(r) = \frac{1}{2}\int_0^\infty \phi(\nu, r) \exp\left[-\int_{r_\mathrm{top}}^{r} \alpha_{\mathrm{L}_{ij}} \phi(\nu, r) dr\right] d\nu, \tag{14}$$

where r_top is the radius of the outer boundary (top of atmosphere), $\alpha_{\mathrm{L}_{ij}}$ is the integrated absorption coefficient, and $\phi(\nu, r)$ is the line profile. Here $\alpha_{\mathrm{L}_{ij}}$ is given by

$$\alpha_{\mathrm{L}_{ij}} = \frac{c^2}{8\pi\nu_{ij}^2} n_{s,i} A_{ij} \left(\frac{n_{s,j} g_i}{n_{s,i} g_j} - 1 \right). \tag{15}$$

Assuming the Doppler profile, $\phi(\nu, r)$ is given by

$$\phi(\nu, r) = \frac{1}{\sqrt{\pi}\Delta\nu_D} \exp\left[-\frac{1}{(\Delta\nu_D)^2} \left(\nu - \nu_0 - \frac{u_s(r)}{c}\nu_0 \right)^2 \right], \tag{16}$$

where $u_s(r)$ is the radial velocity profile of radiative species s and ν_0 is the central frequency of the line profile under no flow. $\Delta\nu_D$ is the doppler width, and it is given by

$$\Delta\nu_D = \frac{\nu_0}{c}\sqrt{\frac{3k_B T}{m_s}}, \tag{17}$$

where m_s is the molecular mass of concerning species s. The net radiative cooling rate q_{rad} is obtained by the sum of contributions by all coolants. We refer to the line data provided by HITRAN database (`http://hitran.org`) and ExoMol databese (`http://exomol.com`). Here we consider the transition of each radiative species described in Section 2 to cover more than 99% of the total energy emission in the temperature range of 100-1000 K. The line emission by H_3^+, OH^+, and H_3O^+ are assumed to be optically thin in the whole calculation region, considering all the lines in the ExoMol database.

S4 Calculation method

The basic equations are solved by numerical time integration until the physical quantities settle into their steady profiles. These equations can be split into advection phases and nonadvection phases. We employ the cubic interpolated profile (CIP) method to solve the advection phases (Yabe and Aoki, 1991) to keep numerical stability and accuracy for hydrodynamic escape simulations (Kuramoto et al., 2013). After solving the advection phases, we solve the nonadvection phases with a finite-difference approach. The nonadvection phases of the energy equation are solved explicitly. Those of the continuity equations are solved with the semi-implicit method. Those of the momentum equations are solved implicitly using the quantities of the next time step that are obtained by the integration of the energy equation and the continuity equations.

On radial coordinates, 1000 numerical grids are taken with the grid-to-grid intervals exponentially increasing with r. The time step is defined to satisfy the Courant-Friedriches-Lewy (CFL) condition. For each parameter setup, we continue the time integration until reaching the steady state using the convergence condition described in Tian et al. (2005). The boundary conditions are described in Section 2. As the initial condition, we use the steady profiles of the pure hydrogen atmosphere and add CO or CO_2 whose number density profiles are given by the hydrostatic structure. The initial velocities of CO and CO_2 are set at 1×10^{-5} m/s regardless of the altitude.

Table S1 Chemical reactions

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R1	$H_2 + h\nu$	$\rightarrow$	$H + H$	
R2		$\rightarrow$	$H_2^+ + e$	
R3		$\rightarrow$	$H^+ + H + e$	
R4	$CH_4 + h\nu$	$\rightarrow$	$CH_2 + H_2$	
R5		$\rightarrow$	$CH_3 + H$	
R6		$\rightarrow$	$CH_2 + H + H$	
R7		$\rightarrow$	$CH_4^+ + e$	
R8		$\rightarrow$	$CH_3^+ + H + e$	
R9		$\rightarrow$	$CH_2^+ + H_2 + e$	
R10		$\rightarrow$	$CH^+ + H_2 + H + e$	
R11		$\rightarrow$	$H^+ + CH_3 + e$	
R12		$\rightarrow$	$CH + H_2 + H$	
R13	$CO + h\nu$	$\rightarrow$	$CO^+ + e$	
R14		$\rightarrow$	$C^+ + O + e$	
R15		$\rightarrow$	$C + O^+ + e$	
R16		$\rightarrow$	$C + O$	
R17		$\rightarrow$	$C + O(^1D)$	
R18	$CO_2 + h\nu$	$\rightarrow$	$CO + O(^1D)$	
R19		$\rightarrow$	$CO_2^+ + e$	
R20		$\rightarrow$	$CO^+ + O + e$	
R21		$\rightarrow$	$O^+ + CO + e$	
R22		$\rightarrow$	$C^+ + O_2 + e$	
R23		$\rightarrow$	$CO + O$	
R24	$CH + h\nu$	$\rightarrow$	$CH^+ + e$	
R25		$\rightarrow$	$C + H$	
R26	$CH_3 + h\nu$	$\rightarrow$	$CH_3^+ + e$	
R27		$\rightarrow$	$CH + H_2$	
R28		$\rightarrow$	$CH_2 + H$	
R29	$H_2O + h\nu$	$\rightarrow$	$H + OH$	
R30		$\rightarrow$	$H_2 + O(^1D)$	
R31		$\rightarrow$	$O + H + H$	
R32		$\rightarrow$	$OH^+ + H + e$	
R33		$\rightarrow$	$O^+ + H_2 + e$	
R34		$\rightarrow$	$H^+ + OH + e$	
R35		$\rightarrow$	$H_2O^+ + e$	
R36	$OH + h\nu$	$\rightarrow$	$O + H$	
R37		$\rightarrow$	$OH^+ + e$	
R38		$\rightarrow$	$O(^1D) + H$	
R39	$O_2 + h\nu$	$\rightarrow$	$O + O$	
R40		$\rightarrow$	$O + O(^1D)$	

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R41		$\rightarrow$	$O^+ + O + e$	
R42		$\rightarrow$	$O_2^+ + e$	
R43	$H + h\nu$	$\rightarrow$	$H^+ + e$	
R44	$C + h\nu$	$\rightarrow$	$C^+ + e$	
R45	$O + h\nu$	$\rightarrow$	$O^+ + e$	
R46	$H_2 + CH$	$\rightarrow$	$C + H_2 + H$	$6.00 \times 10^{-9}\exp(-40200/T)$
R47	$H_2 + CH$	$\rightarrow$	$CH_2 + H$	$5.46 \times 10^{-10}\exp(-1943/T)$
R48	$H_2 + H_2$	$\rightarrow$	$H_2 + H + H$	$1.00 \times 10^{-8}\exp(-84100/T)$
R49	$H_2 + H_2O$	$\rightarrow$	$OH + H_2 + H$	$5.80 \times 10^{-9}\exp(-52900/T)$
R50	$H_2 + O_2$	$\rightarrow$	$O + O + H_2$	$6.00 \times 10^{-9}\exp(-52300/T)$
R51	$H_2 + OH$	$\rightarrow$	$O + H_2 + H$	$6.00 \times 10^{-9}\exp(-50900/T)$
R52	$H_2 + H$	$\rightarrow$	$H + H + H$	$4.67 \times 10^{-7}(T/300)^{-1.00}\exp(-55000/T)$
R53	$H_2 + H_2^+$	$\rightarrow$	$H_3^+ + H$	2.08×10^{-9}
R54	$H_2 + C^+$	$\rightarrow$	$CH^+ + H$	$1.00 \times 10^{-10}\exp(-4640/T)$
R55	$H_2 + C^+$	$\rightarrow$	$CH_2^+ + PHOTON$	$2.00 \times 10^{-16}(T/300)^{-1.30}\exp(-23.00/T)$
R56	$H_2 + CH^+$	$\rightarrow$	$CH_2^+ + H$	1.20×10^{-9}
R57	$H_2 + CH_2^+$	$\rightarrow$	$CH_3^+ + H$	1.60×10^{-9}
R58	$H_2 + CH_4^+$	$\rightarrow$	$CH_5^+ + H$	$4.89 \times 10^{-11}(T/300)^{-0.14}\exp(36.10/T)$
R59	$H_2 + C$	$\rightarrow$	$CH + H$	$6.64 \times 10^{-10}\exp(-11700/T)$
R60	$H_2 + C$	$\rightarrow$	$CH_2 + PHOTON$	1.00×10^{-17}
R61	$H_2 + CH_2$	$\rightarrow$	$CH_3 + H$	$5.18 \times 10^{-11}(T/300)^{0.17}\exp(-6400/T)$
R62	$H_2 + CH_3$	$\rightarrow$	$CH_4 + H$	$6.86 \times 10^{-14}(T/300)^{2.74}\exp(-4740/T)$
R63	$H_2 + CH_3^+$	$\rightarrow$	$CH_5^+ + PHOTON$	$3.92 \times 10^{-16}(T/300)^{-2.29}\exp(-21.30/T)$
R64	$H_2 + CH$	$\rightarrow$	$CH_3 + PHOTON$	$5.09 \times 10^{-18}(T/300)^{-0.71}\exp(-11.60/T)$
R65	$H_2 + H_2O^+$	$\rightarrow$	$H_3O^+ + H$	6.40×10^{-10}
R66	$H_2 + O^+$	$\rightarrow$	$OH^+ + H$	1.70×10^{-9}
R67	$H_2 + OH^+$	$\rightarrow$	$H_2O^+ + H$	1.01×10^{-9}
R68	$H_2 + O_2$	$\rightarrow$	$OH + OH$	$3.16 \times 10^{-10}\exp(-21890/T)$
R69	$H_2 + O$	$\rightarrow$	$OH + H$	$3.14 \times 10^{-13}(T/300)^{2.70}\exp(-3150/T)$
R70	$H_2 + OH$	$\rightarrow$	$H_2O + H$	$2.05 \times 10^{-12}(T/300)^{1.52}\exp(-1736/T)$
R71	$CH_4 + H^+$	$\rightarrow$	$CH_4^+ + H$	1.50×10^{-9}
R72	$CH_4 + H^+$	$\rightarrow$	$CH_3^+ + H_2$	2.30×10^{-9}
R73	$CH_4 + H_2^+$	$\rightarrow$	$CH_4^+ + H_2$	1.40×10^{-9}
R74	$CH_4 + H_2^+$	$\rightarrow$	$CH_3^+ + H_2 + H$	2.30×10^{-9}
R75	$CH_4 + H_2^+$	$\rightarrow$	$CH_5^+ + H$	1.14×10^{-10}
R76	$CH_4 + H_3^+$	$\rightarrow$	$CH_5^+ + H_2$	2.40×10^{-9}
R77	$CH_4 + CH_4^+$	$\rightarrow$	$CH_5^+ + CH_3$	1.50×10^{-9}
R78	$CH_4 + CH_2$	$\rightarrow$	$CH_3 + CH_3$	$7.13 \times 10^{-12}\exp(-5050/T)$
R79	$CH_4 + CO^+$	$\rightarrow$	$CO + CH_4^+$	7.93×10^{-10}
R80	$CH_4 + O^+$	$\rightarrow$	$CH_4^+ + O$	8.90×10^{-10}

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R81	$CH_4 + O^+$	$\rightarrow$	$OH + CH_3^+$	1.10×10^{-10}
R82	$CH_4 + OH^+$	$\rightarrow$	$CH_5^+ + O$	1.95×10^{-10}
R83	$CH_4 + OH^+$	$\rightarrow$	$H_3O^+ + CH_2$	1.31×10^{-9}
R84	$CH_4 + H$	$\rightarrow$	$CH_3 + H_2$	$5.94 \times 10^{-13}(T/300)^{3.0}\exp(-4045/T)$
R85	$CH_4 + CO_2^+$	$\rightarrow$	$CO_2 + CH_4^+$	5.50×10^{-10}
R86	$CH_4 + H_2O^+$	$\rightarrow$	$H_3O^+ + CH_3$	1.40×10^{-9}
R87	$CH_4 + OH$	$\rightarrow$	$H_2O + CH_3$	$3.77 \times 10^{-13}(T/300)^{2.42}\exp(-1162/T)$
R88	$CH_4 + O$	$\rightarrow$	$OH + CH_3$	$2.29 \times 10^{-12}(T/300)^{2.2}\exp(-3820/T)$
R89	$CO + H_2^+$	$\rightarrow$	$CO^+ + H_2$	6.44×10^{-10}
R90	$CO + O^+$	$\rightarrow$	$CO^+ + O$	$4.90 \times 10^{-12}(T/300)^{0.5}\exp(-4580/T)$
R91	$CO + O_2$	$\rightarrow$	$CO_2 + O$	$5.99 \times 10^{-12}\exp(-24075/T)$
R92	$CO + H$	$\rightarrow$	$OH + C$	$1.10 \times 10^{-10}(T/300)^{0.5}\exp(-77700/T)$
R93	$CO + OH$	$\rightarrow$	$CO_2 + H$	$2.81 \times 10^{-13}\exp(-176/T)$
R94	$CO_2 + CO^+$	$\rightarrow$	$CO_2^+ + CO$	1.00×10^{-9}
R95	$CO_2 + C^+$	$\rightarrow$	$CO^+ + CO$	1.10×10^{-9}
R96	$CO_2 + O^+$	$\rightarrow$	$O_2^+ + CO$	9.40×10^{-10}
R97	$CO_2 + H$	$\rightarrow$	$CO + OH$	$3.38 \times 10^{-10}\exp(-13163/T)$
R98	$CO_2 + O$	$\rightarrow$	$O_2 + CO$	$2.46 \times 10^{-11}\exp(-26567/T)$
R99	$CH + H$	$\rightarrow$	$C + H + H$	$6.00 \times 10^{-9}\exp(-40200/T)$
R100	$CH + H$	$\rightarrow$	$C + H_2$	$1.31 \times 10^{-10}\exp(80/T)$
R101	$CH + C^+$	$\rightarrow$	$CH^+ + C$	$3.80 \times 10^{-10}(T/300)^{-0.5}$
R102	$CH + H^+$	$\rightarrow$	$CH^+ + H$	$1.90 \times 10^{-9}(T/300)^{-0.5}$
R103	$CH + H_2^+$	$\rightarrow$	$CH^+ + H_2$	$7.10 \times 10^{-10}(T/300)^{-0.5}$
R104	$CH + H_2^+$	$\rightarrow$	$CH_2^+ + H$	$7.10 \times 10^{-10}(T/300)^{-0.5}$
R105	$CH + CH_5^+$	$\rightarrow$	$CH_2^+ + CH_4$	$6.90 \times 10^{-10}(T/300)^{-0.5}$
R106	$CH + H_3^+$	$\rightarrow$	$CH_2^+ + H_2$	$1.20 \times 10^{-9}(T/300)^{-0.5}$
R107	$CH + CO^+$	$\rightarrow$	$CO + CH^+$	$3.20 \times 10^{-10}(T/300)^{-0.5}$
R108	$CH + O^+$	$\rightarrow$	$O + CH^+$	$3.50 \times 10^{-10}(T/300)^{-0.5}$
R109	$CH + O^+$	$\rightarrow$	$CO^+ + H$	$3.50 \times 10^{-10}(T/300)^{-0.5}$
R110	$CH + OH^+$	$\rightarrow$	$CH_2^+ + O$	$3.50 \times 10^{-10}(T/300)^{-0.5}$
R111	$CH + OH^+$	$\rightarrow$	$OH + CH^+$	$3.50 \times 10^{-10}(T/300)^{-0.5}$
R112	$CH + OH^+$	$\rightarrow$	$O + CH_2^+$	$3.50 \times 10^{-10}(T/300)^{-0.5}$
R113	$CH + H_2O^+$	$\rightarrow$	$H_2O + CH^+$	$3.40 \times 10^{-10}(T/300)^{-0.5}$
R114	$CH + H_2O^+$	$\rightarrow$	$OH + CH_2^+$	$3.40 \times 10^{-10}(T/300)^{-0.5}$
R115	$CH + O_2^+$	$\rightarrow$	$O_2 + CH^+$	$3.10 \times 10^{-10}(T/300)^{-0.5}$
R116	$CH + H_3O^+$	$\rightarrow$	$H_2O + CH_2^+$	$6.80 \times 10^{-10}(T/300)^{-0.5}$
R117	$CH + O_2$	$\rightarrow$	$CO_2 + H$	1.14×10^{-11}
R118	$CH + O_2$	$\rightarrow$	$CO + O + H$	1.14×10^{-11}
R119	$CH + O_2$	$\rightarrow$	$CO + OH$	7.60×10^{-12}
R120	$CH + O$	$\rightarrow$	$CO + H$	$6.02 \times 10^{-11}(T/300)^{0.10}\exp(4.50/T)$

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R121	$CH + O$	$\rightarrow$	$OH + C$	$2.52 \times 10^{-11} \exp(-2381/T)$
R122	$CH_2 + C^+$	$\rightarrow$	$CH_2^+ + C$	5.20×10^{-10}
R123	$CH_2 + H^+$	$\rightarrow$	$CH_2^+ + H$	1.40×10^{-9}
R124	$CH_2 + H^+$	$\rightarrow$	$CH^+ + H_2$	1.40×10^{-9}
R125	$CH_2 + H_2^+$	$\rightarrow$	$CH_2^+ + H_2$	1.00×10^{-9}
R126	$CH_2 + H_2^+$	$\rightarrow$	$CH_3^+ + H$	1.00×10^{-9}
R127	$CH_2 + H_3^+$	$\rightarrow$	$CH_3^+ + H_2$	1.70×10^{-9}
R128	$CH_2 + CH_5^+$	$\rightarrow$	$CH_4 + CH_3^+$	9.60×10^{-10}
R129	$CH_2 + CH_2$	$\rightarrow$	$CH_3 + CH$	$4.00 \times 10^{-10} \exp(-5000/T)$
R130	$CH_2 + H$	$\rightarrow$	$CH + H_2$	2.20×10^{-10}
R131	$CH_2 + C$	$\rightarrow$	$CH + CH$	$2.69 \times 10^{-12} \exp(-23550/T)$
R132	$CH_2 + O$	$\rightarrow$	$CO + H_2$	8.00×10^{-11}
R133	$CH_2 + O$	$\rightarrow$	$CO + H + H$	1.33×10^{-10}
R134	$CH_2 + O$	$\rightarrow$	$OH + CH$	$4.98 \times 10^{-10} \exp(-6000/T)$
R135	$CH_2 + O^+$	$\rightarrow$	$O + CH_2^+$	9.70×10^{-10}
R136	$CH_2 + CO^+$	$\rightarrow$	$CO + CH_2^+$	4.30×10^{-10}
R137	$CH_2 + OH^+$	$\rightarrow$	$O + CH_3^+$	4.80×10^{-10}
R138	$CH_2 + OH^+$	$\rightarrow$	$OH + CH_2^+$	4.80×10^{-10}
R139	$CH_2 + {O_2}^+$	$\rightarrow$	$O_2 + CH_2^+$	4.30×10^{-10}
R140	$CH_2 + H_2O^+$	$\rightarrow$	$OH + CH_3^+$	4.70×10^{-10}
R141	$CH_2 + H_3O^+$	$\rightarrow$	$H_2O + CH_3^+$	9.40×10^{-10}
R142	$CH_2 + O_2$	$\rightarrow$	$CO_2 + H_2$	$2.92 \times 10^{-11} (T/300)^{-3.30} \exp(-1443/T)$
R143	$CH_2 + O_2$	$\rightarrow$	$CO_2 + H + H$	$3.65 \times 10^{-11} (T/300)^{-3.30} \exp(-1443/T)$
R144	$CH_2 + O_2$	$\rightarrow$	$CO + H_2O$	$2.48 \times 10^{-10} (T/300)^{-3.30} \exp(-1443/T)$
R145	$CH_2 + OH$	$\rightarrow$	$CH + H_2O$	$1.44 \times 10^{-11} (T/300)^{0.50} \exp(-3000/T)$
R146	$CH_2 + OH$	$\rightarrow$	$CH_3 + O$	$1.44 \times 10^{-11} (T/300)^{0.50} \exp(-3000/T)$
R147	$CH_3 + H^+$	$\rightarrow$	$CH_3^+ + H$	3.40×10^{-9}
R148	$CH_3 + H_3^+$	$\rightarrow$	$CH_4^+ + H_2$	2.10×10^{-9}
R149	$CH_3 + O$	$\rightarrow$	$CO + H_2 + H$	$3.60 \times 10^{-11} \exp(-202/T)$
R150	$CH_3 + CH_3$	$\rightarrow$	$CH_4 + CH_2$	$7.13 \times 10^{-12} \exp(-5052/T)$
R151	$CH_3 + H_2O$	$\rightarrow$	$OH + CH_4$	$2.30 \times 10^{-15} (T/300)^{3.47} \exp(-6681/T)$
R152	$CH_3 + OH$	$\rightarrow$	$CH_4 + O$	$3.27 \times 10^{-14} (T/300)^{2.20} \exp(-2240/T)$
R153	$CH_3 + OH$	$\rightarrow$	$H_2O + CH_2$	$1.20 \times 10^{-10} \exp(-1400/T)$
R154	$CH_3 + H$	$\rightarrow$	$CH_2 + H_2$	$1.00 \times 10^{-10} \exp(-7600/T)$
R155	$H_2O + H$	$\rightarrow$	$OH + H + H$	$5.80 \times 10^{-9} \exp(-52900/T)$
R156	$H_2O + H^+$	$\rightarrow$	$H_2O^+ + H$	$6.90 \times 10^{-9} (T/300)^{-0.50}$
R157	$H_2O + H_2^+$	$\rightarrow$	$H_2O^+ + H_2$	$3.90 \times 10^{-9} (T/300)^{-0.50}$
R158	$H_2O + CO^+$	$\rightarrow$	$CO + H_2O^+$	$1.72 \times 10^{-9} (T/300)^{-0.50}$
R159	$H_2O + CO_2^+$	$\rightarrow$	$CO_2 + H_2O^+$	$2.04 \times 10^{-9} (T/300)^{-0.50}$
R160	$H_2O + O^+$	$\rightarrow$	$H_2O^+ + O$	$3.20 \times 10^{-9} (T/300)^{-0.50}$

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R161	$H_2O + OH^+$	$\rightarrow$	$H_2O^+ + OH$	$1.59 \times 10^{-9}(T/300)^{-0.50}$
R162	$H_2O + CH^+$	$\rightarrow$	$H_3O^+ + C$	$5.80 \times 10^{-10}(T/300)^{-0.50}$
R163	$H_2O + CH_4^+$	$\rightarrow$	$H_3O^+ + CH_3$	$2.60 \times 10^{-9}(T/300)^{-0.50}$
R164	$H_2O + CH_5^+$	$\rightarrow$	$H_3O^+ + CH_4$	$3.70 \times 10^{-9}(T/300)^{-0.50}$
R165	$H_2O + H_2^+$	$\rightarrow$	$H_3O^+ + H$	$3.40 \times 10^{-9}(T/300)^{-0.50}$
R166	$H_2O + H_2O^+$	$\rightarrow$	$H_3O^+ + OH$	$2.10 \times 10^{-9}(T/300)^{-0.50}$
R167	$H_2O + H_3^+$	$\rightarrow$	$H_3O^+ + H_2$	$5.90 \times 10^{-9}(T/300)^{-0.50}$
R168	$H_2O + OH^+$	$\rightarrow$	$H_3O^+ + O$	$1.30 \times 10^{-9}(T/300)^{-0.50}$
R169	$H_2O + H$	$\rightarrow$	$OH + H_2$	$1.59 \times 10^{-11}(T/300)^{1.20}\exp(-9610/T)$
R170	$H_2O + O$	$\rightarrow$	$OH + OH$	$1.85 \times 10^{-11}(T/300)^{0.95}\exp(-8571/T)$
R171	$OH + H$	$\rightarrow$	$O + H + H$	$6.00 \times 10^{-9}\exp(-50900/T)$
R172	$OH + H$	$\rightarrow$	$H_2O + PHOTON$	$5.26 \times 10^{-18}(T/300)^{-5.22}\exp(-90.00/T)$
R173	$OH + H^+$	$\rightarrow$	$OH^+ + H$	$2.10 \times 10^{-9}(T/300)^{-0.50}$
R174	$OH + H_2^+$	$\rightarrow$	$OH^+ + H_2$	$7.60 \times 10^{-10}(T/300)^{-0.50}$
R175	$OH + O^+$	$\rightarrow$	$OH^+ + O$	$3.60 \times 10^{-10}(T/300)^{-0.50}$
R176	$OH + CO^+$	$\rightarrow$	$CO + OH^+$	$3.10 \times 10^{-10}(T/300)^{-0.50}$
R177	$OH + C^+$	$\rightarrow$	$H + CO^+$	$7.70 \times 10^{-10}(T/300)^{-0.50}$
R178	$OH + CH^+$	$\rightarrow$	$CO^+ + H_2$	$7.50 \times 10^{-10}(T/300)^{-0.50}$
R179	$OH + H_2^+$	$\rightarrow$	$H_2O^+ + H$	$7.60 \times 10^{-10}(T/300)^{-0.50}$
R180	$OH + H_3^+$	$\rightarrow$	$H_2O^+ + H_2$	$1.30 \times 10^{-9}(T/300)^{-0.50}$
R181	$OH + O^+$	$\rightarrow$	$O_2^+ + H$	$3.60 \times 10^{-10}(T/300)^{-0.50}$
R182	$OH + OH^+$	$\rightarrow$	$H_2O^+ + O$	$7.00 \times 10^{-10}(T/300)^{-0.50}$
R183	$OH + CH_5^+$	$\rightarrow$	$H_2O^+ + CH_4$	$7.00 \times 10^{-10}(T/300)^{-0.50}$
R184	$OH + H_2O^+$	$\rightarrow$	$H_3O^+ + O$	$6.90 \times 10^{-10}(T/300)^{-0.50}$
R185	$OH + C$	$\rightarrow$	$CO + H$	1.00×10^{-10}
R186	$OH + C$	$\rightarrow$	$O + CH$	$2.25 \times 10^{-11}(T/300)^{0.50}\exp(-14800/T)$
R187	$OH + H$	$\rightarrow$	$O + H_2$	$6.99 \times 10^{-14}(T/300)^{2.80}\exp(-1950/T)$
R188	$OH + O$	$\rightarrow$	$O_2 + H$	$3.69 \times 10^{-11}(T/300)^{-0.27}\exp(-12.90/T)$
R189	$OH + OH$	$\rightarrow$	$H_2O + O$	$1.65 \times 10^{-12}(T/300)^{1.14}\exp(-50.00/T)$
R190	$O_2 + H$	$\rightarrow$	$O + O + H$	$6.00 \times 10^{-9}\exp(-52300/T)$
R191	$O_2 + CH_4^+$	$\rightarrow$	$O_2^+ + CH_4$	3.90×10^{-10}
R192	$O_2 + CO^+$	$\rightarrow$	$O_2^+ + CO$	1.20×10^{-10}
R193	$O_2 + H^+$	$\rightarrow$	$O_2^+ + H$	2.00×10^{-9}
R194	$O_2 + H_2^+$	$\rightarrow$	$O_2^+ + H_2$	8.00×10^{-10}
R195	$O_2 + H_2O^+$	$\rightarrow$	$O_2^+ + H_2O$	4.60×10^{-10}
R196	$O_2 + O^+$	$\rightarrow$	$O_2^+ + O$	1.90×10^{-11}
R197	$O_2 + CO_2^+$	$\rightarrow$	$CO_2 + O_2^+$	5.30×10^{-11}
R198	$O_2 + OH^+$	$\rightarrow$	$O_2^+ + OH$	5.90×10^{-10}
R199	$O_2 + C^+$	$\rightarrow$	$CO^+ + O$	3.42×10^{-10}
R200	$O_2 + C^+$	$\rightarrow$	$CO + O^+$	4.54×10^{-10}

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R201	$O_2 + CH^+$	$\rightarrow$	$CO^+ + OH$	1.00×10^{-11}
R202	$O_2 + C$	$\rightarrow$	$CO + O$	$5.56 \times 10^{-11}(T/300)^{0.41}\exp(26.90/T)$
R203	$O_2 + H$	$\rightarrow$	$OH + O$	$2.61 \times 10^{-10}(T/300)^{0.41}\exp(-8156/T)$
R204	$H + CO^+$	$\rightarrow$	$CO + H^+$	7.50×10^{-10}
R205	$H + H_2^+$	$\rightarrow$	$H_2 + H^+$	6.40×10^{-10}
R206	$H + CH^+$	$\rightarrow$	$C^+ + H_2$	$9.06 \times 10^{-10}(T/300)^{-0.37}\exp(-29.10/T)$
R207	$H + CH_2^+$	$\rightarrow$	$CH^+ + H_2$	$1.00 \times 10^{-9}\exp(-7080/T)$
R208	$H + CH_3^+$	$\rightarrow$	$CH_2^+ + H_2$	$7.00 \times 10^{-10}\exp(-10560/T)$
R209	$H + CH_4^+$	$\rightarrow$	$CH_3^+ + H_2$	1.00×10^{-11}
R210	$H + CH_5^+$	$\rightarrow$	$CH_4^+ + H_2$	1.50×10^{-10}
R211	$H + CH_2$	$\rightarrow$	$CH + H_2$	2.20×10^{-10}
R212	$H + CH_3$	$\rightarrow$	$CH_2 + H_2$	$1.00 \times 10^{-10}\exp(-7600/T)$
R213	$H + CH_4$	$\rightarrow$	$CH_3 + H_2$	$5.94 \times 10^{-13}(T/300)^{3.00}\exp(-4045/T)$
R214	$H + CH$	$\rightarrow$	$C + H_2$	$1.31 \times 10^{-10}\exp(-80.00/T)$
R215	$H + H^+$	$\rightarrow$	$H_2^+ + \mathrm{PHOTON}$	$1.15 \times 10^{-18}(T/300)^{1.49}\exp(-228.0/T)$
R216	$H + C^+$	$\rightarrow$	$CH^+ + \mathrm{PHOTON}$	1.70×10^{-17}
R217	$H + C$	$\rightarrow$	$CH + \mathrm{PHOTON}$	1.00×10^{-17}
R218	$H + O$	$\rightarrow$	$OH + \mathrm{PHOTON}$	$9.90 \times 10^{-19}(T/300)^{-0.38}$
R219	$H + O^+$	$\rightarrow$	$O + H^+$	$5.66 \times 10^{-10}(T/300)^{0.36}\exp(8.60/T)$
R220	$H + CO^+$	$\rightarrow$	$CO + H^+$	7.50×10^{-10}
R221	$C + CH_5^+$	$\rightarrow$	$CH_4 + CH^+$	1.20×10^{-9}
R222	$C + H_2^+$	$\rightarrow$	$CH^+ + H$	2.40×10^{-9}
R223	$C + H_3^+$	$\rightarrow$	$CH^+ + H_2$	2.00×10^{-9}
R224	$C + CO^+$	$\rightarrow$	$CO + C^+$	1.10×10^{-10}
R225	$C + O_2^+$	$\rightarrow$	$O_2 + C^+$	5.20×10^{-11}
R226	$C + O_2^+$	$\rightarrow$	$CO^+ + O$	5.20×10^{-11}
R227	$C + H_2O^+$	$\rightarrow$	$OH + CH^+$	1.10×10^{-9}
R228	$C + OH^+$	$\rightarrow$	$O + CH^+$	1.20×10^{-9}
R229	$C + O^+$	$\rightarrow$	$CO^+ + \mathrm{PHOTON}$	$5.00 \times 10^{-10}(T/300)^{-3.70}\exp(-800/T)$
R230	$C + O$	$\rightarrow$	$CO + \mathrm{PHOTON}$	$4.69 \times 10^{-19}(T/300)^{1.52}\exp(50.50/T)$
R231	$O + H^+$	$\rightarrow$	$O^+ + H$	$6.86 \times 10^{-10}(T/300)^{0.26}\exp(-224.3/T)$
R232	$O + CO^+$	$\rightarrow$	$CO + O^+$	1.40×10^{-10}
R233	$O + CO_2^+$	$\rightarrow$	$CO_2 + O^+$	9.62×10^{-11}
R234	$O + CO_2^+$	$\rightarrow$	$O_2^+ + CO$	1.64×10^{-10}
R235	$O + CH^+$	$\rightarrow$	$CO^+ + H$	3.50×10^{-10}
R236	$O + H_2^+$	$\rightarrow$	$OH^+ + H$	1.50×10^{-9}
R237	$O + H_3^+$	$\rightarrow$	$H_2O^+ + H$	$3.42 \times 10^{-10}(T/300)^{-0.16}\exp(-1.40/T)$
R238	$O + H_3^+$	$\rightarrow$	$OH^+ + H_2$	$7.98 \times 10^{-10}(T/300)^{-0.16}\exp(-1.40/T)$
R239	$O + CH_4^+$	$\rightarrow$	$OH + CH_3^+$	1.00×10^{-9}
R240	$O + CH_5^+$	$\rightarrow$	$H_3O^+ + CH_2$	2.20×10^{-10}

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R241	$O + CH_5^+$	$\rightarrow$	$H_3O^+ + CH_2$	2.20×10^{-10}
R242	$O + C^+$	$\rightarrow$	$CO^+ + PHOTON$	$3.14 \times 10^{-18}(T/300)^{-0.15}\exp(-68/T)$
R243	$O + H_2O^+$	$\rightarrow$	$O_2^+ + H_2$	4.00×10^{-11}
R244	$O + OH^+$	$\rightarrow$	$O_2^+ + H$	7.10×10^{-10}
R245	$O(^1D)$	$\rightarrow$	O	8.33×10^{-3}
R246	$O(^1D) + H_2O$	$\rightarrow$	$OH + OH$	2.2×10^{-10}
R247	$O(^1D) + H_2$	$\rightarrow$	$H + OH$	1.0×10^{-10}
R248	$O(^1D) + O_2$	$\rightarrow$	$O_2 + O$	$3.2 \times 10^{-11}\exp(70.0/T)$
R249	$O(^1D) + O$	$\rightarrow$	$O + O$	$6.47 \times 10^{-12}(T/300)^{0.14}$
R250	$O(^1D) + CO_2$	$\rightarrow$	$O + CO_2$	$7.4 \times 10^{-11}\exp(120.0/T)$
R251	$O(^1D) + CO$	$\rightarrow$	$O + CO$	3.6×10^{-11}
R252	$O(^1D) + e$	$\rightarrow$	$O + e$	$2.87 \times 10^{-10}(T/300)^{0.91}$
R253	$H^+ + e$	$\rightarrow$	$H + PHOTON$	$3.50 \times 10^{-12}(T/300)^{-0.75}$
R254	$H_2^+ + e$	$\rightarrow$	$H + H$	$1.60 \times 10^{-8}(T/300)^{-0.43}$
R255	$H_3^+ + e$	$\rightarrow$	$H_2 + H$	$2.34 \times 10^{-8}(T/300)^{-0.52}$
R256	$H_3^+ + e$	$\rightarrow$	$H + H + H$	$4.36 \times 10^{-8}(T/300)^{-0.52}$
R257	$C^+ + e$	$\rightarrow$	$C + PHOTON$	$2.36 \times 10^{-12}(T/300)^{-0.29}\exp(17.60/T)$
R258	$CH^+ + e$	$\rightarrow$	$C + H$	$1.50 \times 10^{-7}(T/300)^{-0.42}$
R259	$CH_2^+ + e$	$\rightarrow$	$C + H_2$	$7.68 \times 10^{-8}(T/300)^{-0.60}$
R260	$CH_2^+ + e$	$\rightarrow$	$C + H + H$	$4.03 \times 10^{-7}(T/300)^{-0.60}$
R261	$CH_2^+ + e$	$\rightarrow$	$CH + H$	$1.60 \times 10^{-7}(T/300)^{-0.60}$
R262	$CH_3^+ + e$	$\rightarrow$	$CH_2 + H$	$7.75 \times 10^{-8}(T/300)^{-0.50}$
R263	$CH_3^+ + e$	$\rightarrow$	$CH + H_2$	$1.95 \times 10^{-7}(T/300)^{-0.50}$
R264	$CH_3^+ + e$	$\rightarrow$	$CH + H + H$	$2.00 \times 10^{-7}(T/300)^{-0.40}$
R265	$CH_4^+ + e$	$\rightarrow$	$CH_2 + H + H$	$1.75 \times 10^{-7}(T/300)^{-0.50}$
R266	$CH_4^+ + e$	$\rightarrow$	$CH_3 + H$	$1.75 \times 10^{-7}(T/300)^{-0.50}$
R267	$CH_5^+ + e$	$\rightarrow$	$CH_2 + H_2 + H$	$4.76 \times 10^{-8}(T/300)^{-0.52}$
R268	$CH_5^+ + e$	$\rightarrow$	$CH_3 + H_2$	$1.40 \times 10^{-8}(T/300)^{-0.52}$
R269	$CH_5^+ + e$	$\rightarrow$	$CH_3 + H + H$	$1.96 \times 10^{-7}(T/300)^{-0.52}$
R270	$CH_5^+ + e$	$\rightarrow$	$CH_4 + H$	$1.40 \times 10^{-8}(T/300)^{-0.52}$
R271	$CH_5^+ + e$	$\rightarrow$	$CH + H_2 + H_2$	$8.40 \times 10^{-9}(T/300)^{-0.52}$
R272	$O^+ + e$	$\rightarrow$	$O + PHOTON$	$3.24 \times 10^{-12}(T/300)^{-0.66}$
R273	$CO^+ + e$	$\rightarrow$	$C + O$	$1.8 \times 10^{-7}(T/300)^{-0.48}$
R274	$CO^+ + e$	$\rightarrow$	$C + O(^1D)$	$2.5 \times 10^{-8}(T/300)^{-0.48}$
R275	$CO_2^+ + e$	$\rightarrow$	$CO + O$	$3.80 \times 10^{-7}(T/300)^{-0.50}$
R276	$O_2^+ + e$	$\rightarrow$	$O + O$	$0.22 \times 1.95 \times 10^{-7}(T/300)^{-0.70}$
R277	$O_2^+ + e$	$\rightarrow$	$O + O(^1D)$	$0.42 \times 1.95 \times 10^{-7}(T/300)^{-0.70}$
R278	$O_2^+ + e$	$\rightarrow$	$O(^1D) + O(^1D)$	$0.36 \times 1.95 \times 10^{-7}(T/300)^{-0.70}$
R279	$OH^+ + e$	$\rightarrow$	$O + H$	$3.75 \times 10^{-8}(T/300)^{-0.50}$
R280	$OH^+ + e$	$\rightarrow$	$O(^1D) + H$	$3.94 \times 10^{-8}(T/300)^{-1.28}$

Ref. McElroy et al. (2013)

Table S1 Chemical reactions (continued)

No.	Reaction			Reaction rate $cm^3\,s^{-1}$
R281	$H_2O^+ + e$	$\rightarrow$	$O + H_2$	$3.90 \times 10^{-8}(T/300)^{-0.50}$
R282	$H_2O^+ + e$	$\rightarrow$	$O + H + H$	$3.05 \times 10^{-7}(T/300)^{-0.50}$
R283	$H_2O^+ + e$	$\rightarrow$	$OH + H$	$8.60 \times 10^{-8}(T/300)^{-0.50}$
R284	$H_3O^+ + e$	$\rightarrow$	$H_2O + H$	$7.09 \times 10^{-8}(T/300)^{-0.50}$
R285	$H_3O^+ + e$	$\rightarrow$	$O + H_2 + H$	$5.60 \times 10^{-9}(T/300)^{-0.50}$
R286	$H_3O^+ + e$	$\rightarrow$	$OH + H_2$	$5.37 \times 10^{-8}(T/300)^{-0.50}$
R287	$H_3O^+ + e$	$\rightarrow$	$OH + H + H$	$3.05 \times 10^{-7}(T/300)^{-0.50}$
				Ref. McElroy et al. (2013)