

The Role of Hydrocarbons in the Ionospheres of the Outer Planets

S. K. ATREYA AND T. M. DONAHUE

*Department of Atmospheric and Oceanic Science, University of Michigan,
Ann Arbor, Michigan 48105*

Received December 9, 1974

The role of hydrocarbons as a possible sink for H^+ and H_3^+ ions in the lower ionosphere of the outer planets is examined. Calculations indicate that H^+ and H_3^+ are efficiently converted to hydrocarbon ions on reaction with methane. The terminal ions, CH_5^+ and $C_2H_5^+$ are rapidly neutralized in dissociative recombination with electrons. Extreme ultraviolet photolysis of hydrocarbons as a potential additional source of lower elevation ions is investigated.

INTRODUCTION

McElroy (1973) first raised the possibility that protons in the Jovian ionosphere may be efficiently removed at lower altitudes by reaction with methane. In our last paper on the model ionospheres of Saturn, Uranus and Neptune (Atreya and Donahue, 1975) we mentioned that H^+ and H_3^+ would rapidly combine with CH_4 to form CH_5^+ and $C_2H_5^+$ if the reaction rates were comparable to the gas kinetic rates. The recently measured values of rate constants for hydrocarbon reactions with H^+ , H_3^+ , and H^+ (Huntress, 1975) confirm our suspicions. In this follow-up note we present the result of calculations based on a chemical model which takes into consideration such hydrocarbon reactions. Results are first presented for Saturn and potential ionization processes at lower elevations for both Saturn and Jupiter are discussed. As we mentioned earlier (Atreya and Donahue, 1975) the methane mixing ratio on Uranus and Neptune is not firmly established yet, therefore we exclude these planets from our present discussion. The model calculations, however, are general and can be easily extended to these other outer planets.

MODELS

We adapt a medium K (eddy diffusion coefficient, $K = 2 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$) neutral

model atmosphere for Saturn as we did in our last paper (Atreya and Donahue, 1975). This is done for the sake of consistency and because the value of K is quite uncertain. The chemical model is presented in Table I. All reactions other than those with the hydrocarbons are taken from Atreya and Donahue (1975). Hinteregger (1970) solar euv fluxes were scaled to the planet, and divided by a factor of two to construct diurnal average models. A solar zenith angle of 60° was assumed and the wavelength interval between 0 and 960 \AA was divided into grids of 5 \AA size; appropriate cross-sections were averaged in the grid interval. References for the cross-sections are found elsewhere (McElroy, 1973). Ion densities calculated under assumptions of photochemical equilibrium are shown in Fig. 1. One notes, as before (Atreya and Donahue, 1975), that H^+ is the dominant ion above 160 km. In this region removal of H^+ takes place principally by electron recombination. Below 160 km, conversion of H^+ to H_3^+ by three-body association reaction (e10) begins to be significant. Below 140 km, methane begins to play a major role in converting H_3^+ (and the remaining H^+) to the hydrocarbon ions. There is a sharp switchover in role as major and minor ions from H_3^+ and H^+ to $C_2H_5^+$ and CH_5^+ . $C_2H_5^+$ and CH_5^+ are rapidly neutralized on dissociative recombination with electrons (r6 and r7).

TABLE I
 IMPORTANT REACTIONS IN THE IONOSPHERES OF THE OUTER PLANETS

Reaction number	Reaction	Rate constant ^a	Reference
Ion production:			
p1	$H_2 + h\nu \rightarrow H_2^+ + e$		
p2	$\rightarrow H^+ + H + e$		
p3	$H_2 + e \rightarrow H_2^+ + 2e$		
p4	$\rightarrow H^+ + H + 2e$		McElroy (1973)
p5	$H + h\nu \rightarrow H^+ + e$		
p6	$H + e \rightarrow H^+ + 2e$		
p7	$He + h\nu \rightarrow He^+ + e$		
p8	$He + e \rightarrow He^+ + 2e$		
Ion exchange:			
e1	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.0×10^{-9}	
e2	$H_2^+ + H \rightarrow H_2 + H^+$	$\sim 1.0 \times 10^{-10}$	
e3	$He^+ + H_2 \rightarrow He + H_2^+$	$\approx 20\%$	Atreya and Donahue (1975)
e4	$\rightarrow HeH^+ + H$	1.0×10^{-13}	} sum
e5	$\rightarrow He + H + H^+$	$\approx 80\%$	
e6	$He^+ + CH_4 \rightarrow CH^+ + H_2 + H + He$	2.4×10^{-10}	
e7	$\rightarrow CH_2^+ + H_2 + He$	9.3×10^{-10}	
e8	$\rightarrow CH_3^+ + H + He$	6.3×10^{-11}	Huntress (1975)
e9	$\rightarrow CH_4^+ + He$	3.8×10^{-11}	
e10	$H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2$	3.2×10^{-29}	Atreya and Donahue (1975)
e11	$H^+ + CH_4 \rightarrow CH_3^+ + H_2$	2.3×10^{-9}	Huntress (1975)
e12	$\rightarrow CH_4^+ + H$	1.5×10^{-9}	
e13	$HeH^+ + H_2 \rightarrow H_3^+ + He$	1.85×10^{-9}	Atreya and Donahue (1975)
e14	$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2$	2.4×10^{-9}	
e15	$CH^+ + H_2 \rightarrow CH_2^+ + H$	1.0×10^{-9}	
e16	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	7.2×10^{-10}	
e17	$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	9.5×10^{-10}	Huntress (1975)
e18	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	1.15×10^{-9}	
e19	$CH_4^+ + H_2 \rightarrow CH_5^+ + H$	4.1×10^{-11}	
Ion removal/electron-ion recombination:			
r1	$H_3^+ + e \rightarrow H_2 + H$	3.8×10^{-7}	
r2	$H_2^+ + e \rightarrow H + H$	$< 1.0 \times 10^{-8}$	
r3	$HeH^+ + e \rightarrow He + H$	$\sim 1.0 \times 10^{-8}$	Atreya and Donahue (1975)
r4	$H^+ + e \rightarrow H + h\nu$	6.6×10^{-12}	
r5	$He^+ + e \rightarrow He + h\nu$	6.6×10^{-12}	
r6	$CH_5^+ + e \rightarrow$	1.9×10^{-6}	Rebbert <i>et al.</i> (1973)
r7	$C_2H_5^+ + e \rightarrow$	1.9×10^{-6}	Rebbert <i>et al.</i> (1973)

^a The rate constants are in units of $cm^3 sec^{-1}$ for two-body reactions, and $cm^6 sec^{-1}$ for three-body reactions.

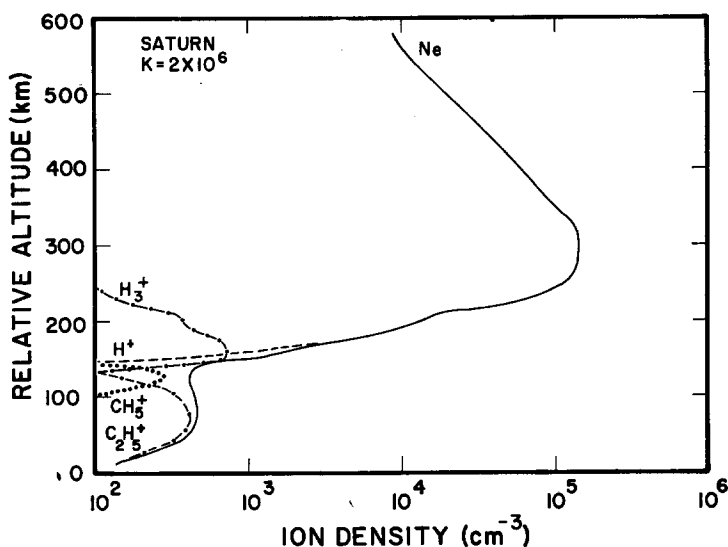


FIG. 1. A model for Saturn's ionosphere with eddy diffusion coefficient, $K = 2 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$. The vertical scale gives the height above a reference level where the hydrogen density is $10^{16} \text{ molecules cm}^{-3}$.

DISCUSSION

Calculations indicate that CH_4 provides an important sink for H^+ and H_3^+ ions up to an altitude just above the methane turbopause. The important ions in this region are C_2H_5^+ and CH_5^+ . Hydrocarbons other than methane are not found to be important sinks of H^+ and H_3^+ . Strobel (1975) pointed out the potential importance of euv photolysis of CH_4 which results in CH_4^+ and CH_3^+ ions below 945 \AA . Our calculations reveal that the absorption by H_2 in this region of the spectrum is so large that methane photoionization contributes no more than 3% to the electron density. Strobel (personal communication, 1974) also estimates an upper limit of $2 \times 10^{-17} \text{ cm}^2$ for the value of photoionization cross-section of CH_3 , whose measured ionization potential is $9.82 \pm 0.04 \text{ eV}$ (Elder *et al.*, 1962). Solar $\text{Ly } \alpha$ is expected to be the principal ionizing flux for this methyl radical. Ionization from radiation other than $\text{Ly } \alpha$ should be insignificant. For Saturn, crude hydrocarbon models with $K = 2 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$ give a value of CH_3 much too low for it to cause any visible change in the electron density profile due to CH_3^+ ion production. However, for purposes of illustration, we

show, in Fig. 2, Jupiter's electron density profiles assuming Strobel's (1975) $K = 10^5$ (low K) and $K \propto 1/(M)^{1/2}$ (high K ; $K = 3 \times 10^7$ at the turbopause) hydrocarbon models. The discussion of location and magnitude of the electron density maxima in the low and high K models is found elsewhere (Atreya *et al.*, 1974). Here we simply wish to illustrate the influence of CH_3^+ production on the ionospheric profile based on the chemical model listed in Table I. It can be seen that the CH_3^+ production peaks at an altitude where CH_3 maxima occur and where optical depth in methane is about 0.3. CH_3^+ production drops off sharply below the maximum because of onset of intense absorption of radiation in methane. CH_3^+ ions are quickly converted to C_2H_5^+ ions (e17). The lower altitude peak in the electron density profile corresponds to this CH_3^+ ion production. The major ion here is C_2H_5^+ . We emphasize, however, that CH_3^+ ion production is purely conjectural and no experimental data or conclusive theoretical estimates of its ionization cross-section and quantum yield are yet available. Maximum $p[\text{CH}_3^+]$ are $1.2 \text{ cm}^{-3} \text{ sec}^{-1}$ and $13 \text{ cm}^{-3} \text{ sec}^{-1}$ for $K = 10^5$ and $K \propto M^{-1/2}$ models, respectively; corres-

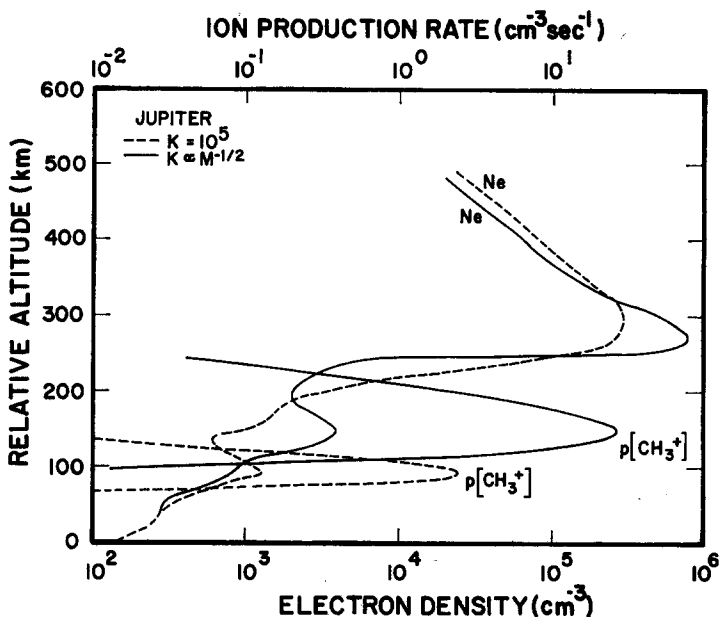


FIG. 2. Jupiter's model ionosphere with $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$ and $K \propto M^{-1/2}$. CH_3^+ ion production rates, $p[\text{CH}_3^+]$, for the two models are given by the upper scale. Height scale is the same as in Fig. 1.

ponding Ne at these altitudes are 10^3 cm^{-3} and $2.8 \times 10^3 \text{ cm}^{-3}$. The secondary ion peak due to CH_3^+ is also dependent upon the value of dissociative recombination coefficient, r_7 ; a value of r_7 twice as large as the one given by Rebbert *et al.* (1973) will essentially wipe out this feature. Improved measurements of r_6 and r_7 are urgently needed.

Discrepancies between the Pioneer 10 results and a pure photochemical ionospheric model involving H, H_2 , He, and hydrocarbons but neglecting the possible role of metallic ions and wind shear sporadic E -like layering exist and were foreseen as possibilities in the paper by Atreya *et al.* (1974). The mechanisms producing large ion peaks below the principal F region peak are being investigated.

ACKNOWLEDGMENTS

We thank Darrell F. Strobel for supplying us with his Jovian hydrocarbon models and for discussion on the euV photolysis of hydrocarbons. This research was supported in part by

the Kitt Peak National Observatory grant AURA-86-303 to the University of Michigan.

REFERENCES

- ATREYA, S. K., AND DONAHUE, T. M. (1975). Ionospheric models of Saturn, Uranus and Neptune. *Icarus* **24**, 358.
- ATREYA, S. K., DONAHUE, T. M., AND McELROY, M. B. (1974). Jupiter's ionosphere: Prospects for Pioneer 10. *Science* **184**, 154.
- ELDER, F. A., GEISE, C., STEINER, B., AND INGRAM, M. (1962). Photo-ionization of alkyl free radicals. *J. Chem. Phys.* **36**, 3292.
- HINTEREGGER, H. E. (1970). The extreme ultraviolet solar spectrum and its variation during solar cycle. *Ann. Geophys.* **26**, 547.
- HUNTRESS, W. T., JR. (1975). A review of Jovian ionospheric chemistry. *Adv. At. Mol. Phys.* **10**, 295.
- McELROY, M. B. (1973). The ionospheres of the major planets. *Space Sci. Rev.* **14**, 460.
- REBBERT, R. E., LIAS, S. G., AND AUSLOOS, P. (1973). Pulse radiolysis of methane. *J. Res. Nat. Bur. Std.* **77A**, 249.
- STROBEL, D. F. (1975). Aeronomy of the major planets: Photochemistry of ammonia and hydrocarbons. *Rev. Geophys. Space Phys.* **13**, in press.