HYDROCARBON IONS IN THE IONOSPHERES OF TITAN AND JUPITER

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ABSTRACT

Two examples are given of models of ion chemistry in reducing atmospheres: Titan, which is a satellite of Saturn, and Jupiter, the largest of the gas giants. In both ionospheres, layers of hydrocarbon and/or C, H, and N-containing ions have been predicted to appear, with larger ions dominating at lower altitudes. Altitude profiles are presented for individual C_1- and C_2-hydrocarbon ions and larger ions that are represented for example, as $C_xH_y^+$ and $C_xH_yN_z^+$. The accuracy of the predictions is, however, limited by the availability of information about the chemistry of these ions. In addition to rate coefficients and product channels for ion-molecule reactions, dissociative recombination coefficients and branching ratios are needed for many hydrocarbon and and related ions.

1. Introduction

Solar ionizing photons are absorbed in the thermospheres of planets and satellites, and the peak ionization rate is usually found at a column density of about $10^{17}\,cm^{-2}$. This altitude may be near or above the homopause, where the transition from transport by large scale mixing to that by molecular diffusion takes place. On Jupiter the peak ionization rate occurs almost 200 km above the homopause, where the major constituents are H_2 and H. Although the density of CH_4 eventually exceeds that of N_2 at high altitudes on Titan, the ionization peak appears just above the homopause, which is near 1050 km. N_2 is the major species at the homopause, and the mixing ratio of CH_4 is 2–10%. Although hydrocarbon and related ions comprise only a small fraction of the ions produced on Jupiter and Titan, models show that such ions may be abundant near or below the major ion peaks in both ionospheres.

The major ions produced in any ionosphere will be transformed by ion-neutral reactions if they are formed in the presence of sufficient densities of neutrals with which they can react. In reducing environments, such as the atmospheres of the outer planets and their satellites, ionization tends to flow from species whose parent neutrals have small proton affinities to species whose parent neutrals have large proton affinities. On the giant planets, the terminal ions will be large protonated hydrocarbons; on Titan, the major species will be both hydrocarbon ions and protonated nitriles and amines. In most cases, the available information about ion chemistry is insufficient to identify the terminal ions in the bottomside ionospheres, but since larger molecules tend to have larger proton affinities, the average size of the ion probably increases

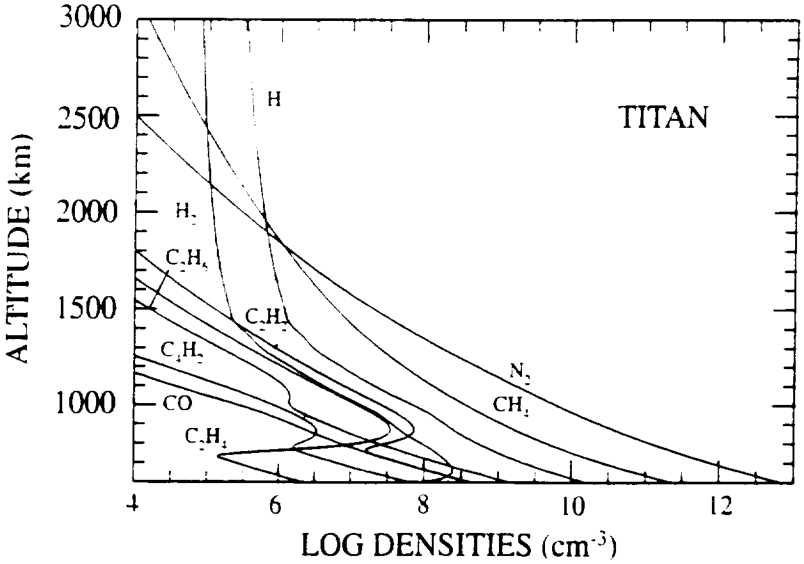

Fig. 1. Density profiles of neutral species in the Titan ionosphere.

with decreasing altitude. In order to improve our understanding of these ionospheres, rate coefficients and branching ratios for reactions of hydrocarbons and hydrocarbon ions, and neutral and ionic species containing C, H and N are needed, including those for dissociative recombination reactions.

2. Titan

In addition to N_2 and CH_4, the thermosphere of Titan contains significant densities of H_2, H, and non-methane hydrocarbons. The background model neutral thermosphere that we have adopted here is shown in Fig. 1. The density profiles of N_2 and CH_4 are taken from Strobel et al. (1992), and those of C_2H_2, C_2H_4, C_2H_6, and C_4H_2 are taken from Yung et al. (1984). The mixing ratio of methane assumed in the model is 3%. The CO mixing ratio is adopted from the ground-based measurements of Gurwell and Muhleman (1995). In our model, we compute the densities of 31 neutral species and 37 ions, the most important of which are N_2^+, N_2H^+, H_3^+, $HCNH^+$, C_1- and C_2- hydrocarbon ions, $C_4H_3^+$, and two pseudo-ions called $C_xH_y^+$ and $C_xH_yN_z^+$, which represent, respectively, hydrocarbon ions other than those included explicitly, and ions containing C, H, and N (formed, for example, from nitriles and amines).

We have included photoabsorption and photoionization of N_2, CH_4, C_2H_2, C_2H_4, C_2H_6, N, C, H and H_2, photodissociation of HCN, and photoionization of CH_3 by Lyman alpha. The solar spectrum used is the high solar activity F79050N spectrum of Hinteregger (private communication), and the solar zenith angle is 60°. Photoelectron-impact ionization was included for N_2, CH_4, H, H_2, N and C. The most important production rate profiles are shown in Fig. 2. The major ion produced is N_2^+ from 600 to 1800 km, and CH_4^+ above that altitude. Other important

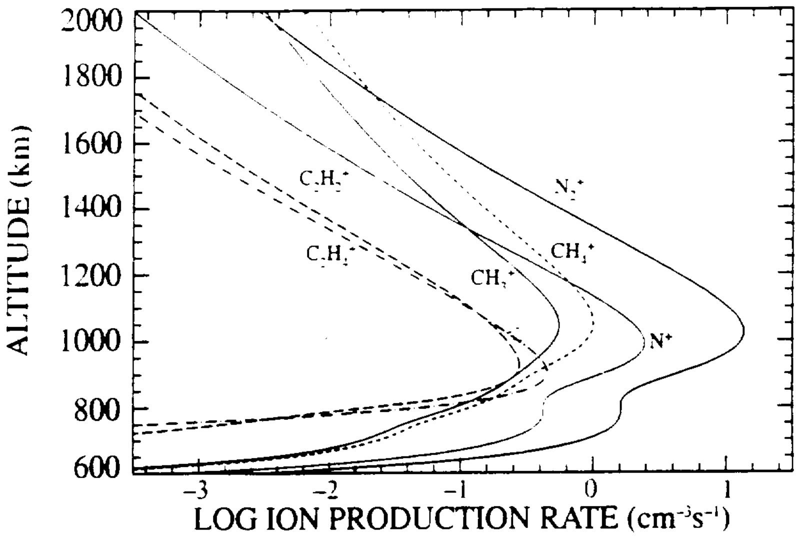

Fig. 2. Ion production rate profiles in the Titan ionosphere (Fox and Yelle, unpublished).

ions produced include N^+, CH_3^+, $C_2H_2^+$, and $C_2H_4^+$.

The ion density profiles were computed including 627 chemical reactions, eddy and molecular diffusion for neutrals, and ambipolar diffusion of ions. Most of the rate coefficients for the ion-molecule reactions were taken from the compilations of Anicich and Huntress (1986) and Anicich (1993). For neutral-neutral reactions, rate coefficients were taken from the model of Yung et al. (1984) or from models of the interstellar medium (e.g., Millar et al., 1988). The most important dissociative recombination coefficients and their sources are shown in Table 1; where no measurements are available, values of $(3 - 3.5) \times 10^{-7}(300/T_e)^{0.5}$ $cm^3 s^{-1}$ were assumed. Even where dissociative recombination coefficients have been measured, in many cases there is little information about the product yields, for which in general there are many possibilities, especially for polyatomic ions. Because the ion and neutral chemistries are coupled, and because the exothermicity and production of fast atoms depend on the channel by which the recombination proceeds, measurements of the product yields are important. Here we have assumed that the available channels are populated with equal probability.

The predicted densities of the major ions are shown in Fig. 3. The major ion at high altitudes is N_2H^+, and from 1300–1800 km, it is $C_2H_5^+$. At the peak the dominant ion is the pseudo-ion $C_xH_y^+$. The density of $C_4H_3^+$ exceeds that of $C_xH_y^+$ near its peak at about 750 km. Most other models have predicted that $HCNH^+$ would be the major ion (Ip, 1990; Keller et al., 1992; Keller and Cravens, 1994). Our model shows that $HCNH^+$ is lost by reaction with C_4H_2, HC_3N, and NH_3 below 1000 km, and by dissociative recombination above that altitude. The most important production reactions for $C_xH_y^+$ are reactions of C_1- and C_2- hydrocarbon ions with acetylene, C_2-hydrocarbon ions with methane and a few reactions of C_1- or C_2- hydrocarbon ions

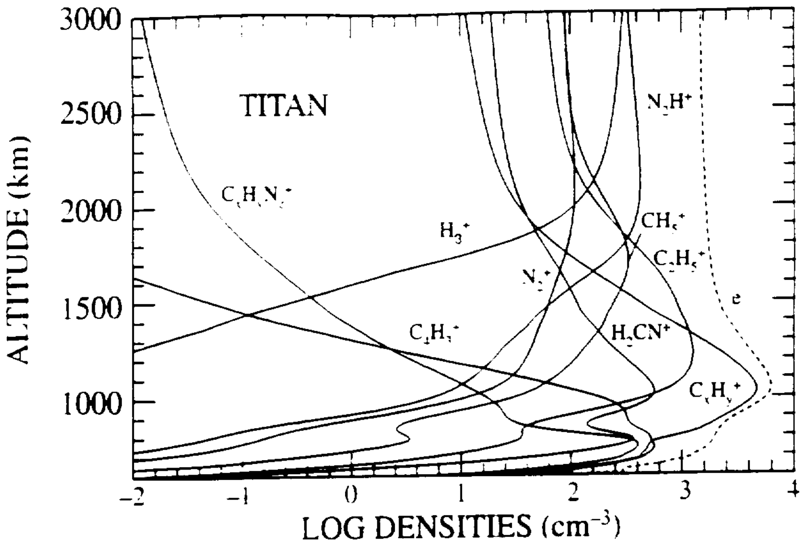

Fig. 3. Predicted ion density profiles in the Titan ionosphere (Fox and Yelle, unpublished).

with ethylene and ethane. Although $C_xH_y^+$ clearly does not represent a single ion, the computed peak density of $HCNH^+$ is almost an order of magnitude less than the total electron density.

Clearly, a major uncertainty in the ionosphere model is the accuracy of the neutral model, including the density profiles computed by Yung et al. (1984). The conclusion that $HCNH^+$ does not dominate the ion density profile, however, depends only on the presence (with a large enough density) of some species that has a higher proton affinity than HNC or HCN, or of some other chemical pathway to the protonated species. With a fairly thermospheric large mixing ratio of methane, and the presence of solar ultraviolet photons, that is all but certain.

3. Jupiter

On Jupiter, the major constituents of the thermosphere are H_2 and H, but below the homopause, which is about 440 km above the ammonia cloud tops, a small but significant amount of methane, about 0.001 – 0.01%, is present (e.g., Atreya, 1986). The models of Kim and Fox (1991; 1994) have shown that, although the peak ion production is near 600 km, ultraviolet photons in the wings of the molecular hydrogen absorption lines penetrate to below the methane homopause, producing significant ionization of C_1- and C_2-hydrocarbon ions, as shown in Fig. 4. These ions are converted to larger hydrocarbon ions with very little loss by recombination. A hydrocarbon ion layer forms below the H^+ and H_3^+ peaks, in the region 300–400 km above the ammonia cloud tops. Altitude profiles of the major hydrocarbon ions at local noon are shown in Fig. 5. Insufficient information about the chemistry is known to track the evolution of larger hydrocarbon molecules, and two pseudo-ions $C_3H_n^+$

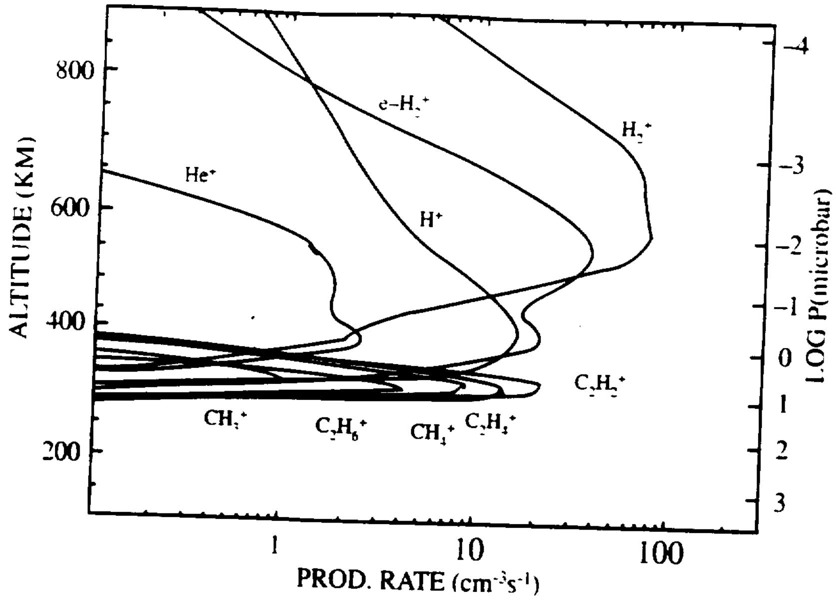

Fig. 4. Ion production rate profiles in the Jovian ionosphere (Kim and Fox, 1994).

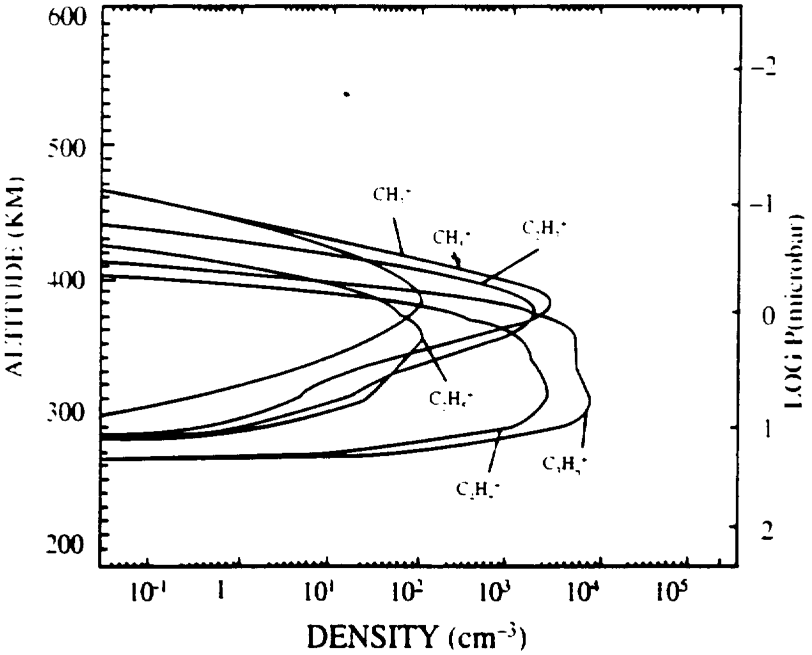

Fig. 5. Predicted hydrocarbon ion density profiles in the Jovian ionosphere. The H^+ and H_3^+ profiles peak at higher altitudes and are not shown (Kim and Fox, 1994).

Table 1. Assumed Dissociative Recombination Coefficients

Species	Rate Coefficient ($cm^3\,s^{-1}$)	Reference
CH^+	$1 \times 10^{-7}(300/T_e)^{0.42}$	Mitchell and McGowan (1978)
CH_2^+	$2.5 \times 10^{-7}(300/T_e)^{0.5}$	Mul et al. (1981)
CH_3^+	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	Mul et al. (1981)
CH_4^+	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	Mul et al. (1981)
CH_5^+	$11 \times 10^{-7}(300/T_e)^{0.5}$	Adams et al. (1984; 1991)
C_2^+	$3 \times 10^{-7}(300/T_e)^{0.5}$	Mul et al. (1981)
C_2H^+	$2.7 \times 10^{-7}(300/T_e)^{0.5}$	Mul and McGowan (1980)
$C_2H_2^+$	$2.7 \times 10^{-7}(300/T_e)^{0.5}$	Mul and McGowan (1980)
$C_2H_3^+$	$4.5 \times 10^{-7}(300/T_e)^{0.5}$	Mul and McGowan (1980)
$C_2H_4^+$	$3 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_2H_5^+$	$7.4 \times 10^{-7}(300/T_e)^{0.5}$	Adams and Smith (1988)
$C_2H_6^+$	$3 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_2H_7^+$	$(3.0 - 3.5) \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_3H_n^+$	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_4H_n^+$	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_xH_y^+$	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_xH_yN_z^+$	$5.0 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$HCNH^+$	$3.5 \times 10^{-7}(300/T_e)^{0.5}$	Adams and Smith (1988)
CN^+	$3 \times 10^{-7}(300/T_e)^{0.5}$	estimate
C_2N^+	$3.0 \times 10^{-7}(300/T_e)^{0.5}$	estimate
$C_4H_3^+$	$6.2 \times 10^{-7}(300/T_e)^{0.5}$	Adams and Smith (1988)
NH^+	$0.43 \times 10^{-7}(300/T_e)^{0.5}$	Mitchell (1990)
NH_2^+	$3 \times 10^{-7}(300/T_e)^{0.5}$	Mitchell (1990)
NH_3^+	$3.3 \times 10^{-7}(300/T_e)^{0.5}$	Mitchell (1990)
NH_4^+	$11 \times 10^{-7}(300/T_e)^{0.9}$	DuBois et al. (1978)
N_2H^+	$1.7 \times 10^{-7}(300/T_e)^{0.5}$	Adams et al. (1984: 1991)

and $C_4H_n^+$ were used to represent ions with three and four C atoms, respectively, and subsequent ions in the evolutionary sequence. Although CH_5^+ and $C_2H_5^+$ dominate on the topside of the layer, at lower altitudes the ions are converted to larger hydrocarbon ions. A more detailed model will require more information about ion-molecule and dissociative recombination reactions of many hydrocarbon ions.

4. Acknowledgements

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