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Review

The Composition and Chemistry of Titan's Atmosphere

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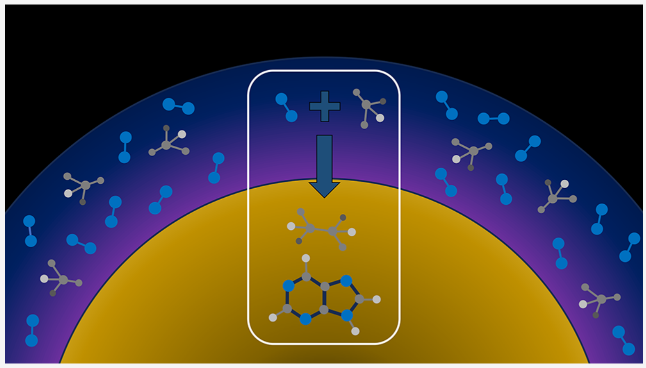
ABSTRACT: In this review I summarize the current state of knowledge about the composition of Titan's atmosphere and our current understanding of the suggested chemistry that leads to that observed composition. I begin with our present knowledge of the atmospheric composition, garnered from a variety of measurements including *Cassini−Huygens*, the *Atacama Large Millimeter/submillimeter Array*, and other ground- and space-based telescopes. This review focuses on the typical vertical profiles of gases at low latitudes rather than global and temporal variations. The main body of the review presents a chemical description of how complex molecules are believed to arise from simpler species, considering all known "stable" molecules—those that have been uniquely identified in the neutral atmosphere. The last section of the review is devoted to the gaps in our present knowledge of Titan's chemical composition and how further work may fill those gaps.



KEYWORDS: *Titan, Astrochemistry, Astrobiology, Atmospheres, Photochemistry*

■ INTRODUCTION

Titan, Saturn's largest moon, was first observed in 1655 by the Dutch astronomer Christiaan Huygens. This important discovery that Saturn, in addition to Jupiter, had its own satellite helped to consolidate the Copernican worldview: that the Earth was no longer to be considered the center of the Solar System but rather one of several planets orbiting the Sun and possessing natural satellites of their own. In his excitement at this new finding, Huygens would have little suspected what would transpire 350 years later: that a machine devised and launched into the heavens by humanity and bearing his name would traverse an unimaginable void and then land softly on his new world, finding it stranger and more alien than even the machine's designers had anticipated.[1]

Over the 13 years from 2004 to 2017, the *Cassini−Huygens* mission[2,3] was able to significantly reveal Titan, both to our eyes and to our minds. Between the successful landing of the ESA-built *Huygens* probe carrying six scientific suites in January 2005 and the 127 flybys of the NASA-built *Cassini* spacecraft with its own 12 science instruments, our knowledge of Titan now is vastly greater than before the mission arrived. So, in our privileged position of hindsight, what do we now know about Titan, almost four centuries since its discovery?

First and foremost, it is a moon with a dense atmosphere (Figure 1), the only such body known in our Solar System. Also, this atmosphere, composed primarily of molecular nitrogen and methane, is a largely anoxic environment, with little oxygen to cause the termination of complex organic reactions. The result is a chemical wonderland, with a breathtaking array of complex organic molecules, of which we presently have only the most rudimentary understanding. Figure 2 shows a schematic overview of the presumed chemistry that occurs in Titan's upper atmosphere, where the "raw ingredients" of its photochemical reactions, N_2 and CH_4, are broken apart and recombined into successively larger molecules and finally haze particles.

Titan is a world that is today both tantalizingly more known and more unknown than ever before. Our direct investigations of its atmosphere by the *Huygens* lander and *Cassini* spacecraft have both increased our understanding of Titan enormously and also multiplied our questions. Significant outstanding questions include:

- Why is Titan the only moon in the Solar System with a significant atmosphere, and how did it come to be in its present state?
- Is the atmosphere today in a steady state, or is it growing or shrinking or changing in some way?
- To what degree has the atmosphere interacted with and shaped the surface and subsurface?

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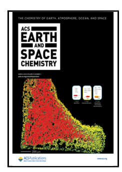

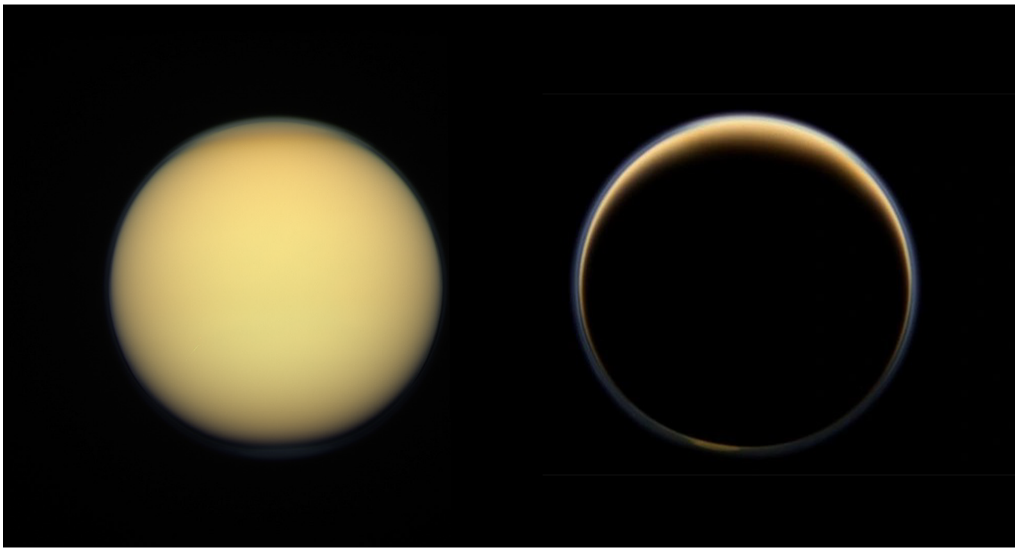

Figure 1. Atmosphere of Titan seen by *Cassini*'s Imaging Science Subsystem (ISS). The dayside image (December 16, 2011) shows Titan's ubiquitous golden haze, opaque to visible light. A darker haze collar is seen around the north pole, along with fainter haze hoods over both the north and south poles, thought to be created by the interaction between chemical and dynamical processes. The nightside image (PIA14924, June 6, 2012, range: 216,000 km) clearly shows the detached atmospheric haze surrounding the entire limb and an elevated stratospheric condensate cloud over the south pole, thought to be composed at least partly of HCN. Image credit: NASA/JPL-Caltech/Space Science Institute/CICLOPS, with reprocessing by Kevin M. Gill.

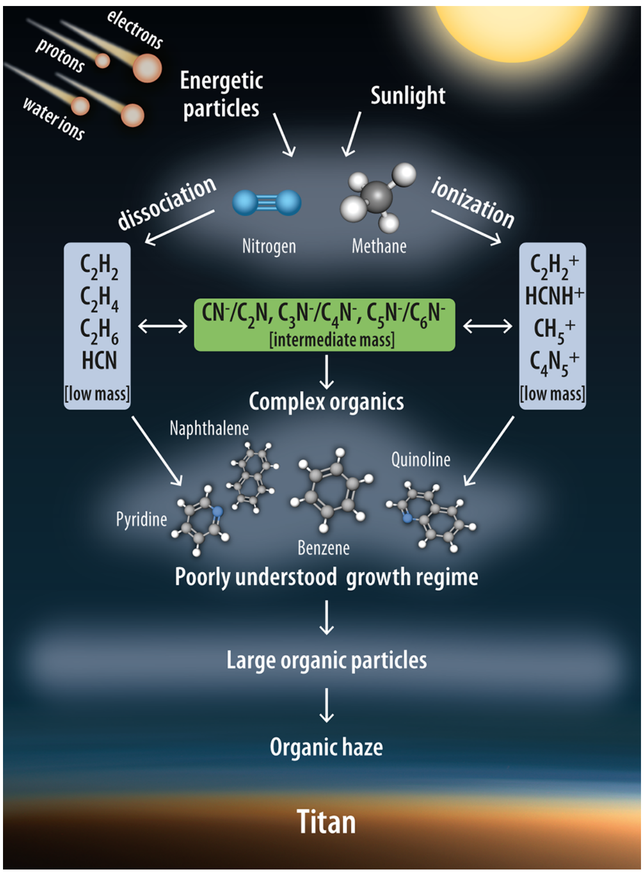

Figure 2. Simplified portrayal of Titan's atmospheric photochemistry, showing the presumed progression from simpler molecules (CH_4, N_2) to more complex molecules and eventually haze particles that can sediment out from the atmosphere. Image adapted from ESA graphic.

- What degree of chemical complexity is reached in Titan's atmosphere, and are precursor biomolecules among the products?
- Are there other moons with atmospheres similar to Titan's elsewhere in the galaxy?

Achieving a better understanding of Titan's atmosphere and its chemistry is important both for the sake of Titan science itself and because of its potential to inform us about other environments. This includes the present-day Earth, since Titan and Earth are the only objects in the Solar System today to have a hydrological cycle of evaporation, condensation, and precipitation and associated rivers, lakes, and seas.[4−7] Like Earth, Titan also experiences seasons, due to orbiting close to Saturn's equatorial plane, which is tilted ∼27° to the ecliptic. Titan therefore experiences summer and winter in each hemisphere, seasons that last ∼7.4× longer than on Earth, with transitional equinox periods of equal daylight at all latitudes.

We also note the relevance to the early Earth, which likely had a much more chemically reducing atmosphere in its distant past,[8−13] before the Great Oxidation Event.[14−16] Finally we can surmise the likely relevance to exoplanets, which vastly outnumber the planets in our own Solar System and more likely than not include Titan-like bodies somewhere in our galaxy.[17−19]

In this review, I attempt to lay out a simple picture of the known characteristics of Titan's atmosphere, with a focus on the composition and chemistry of the dense lower atmosphere. By necessity, this review will not cover, except in passing, many related areas: the origin of the atmosphere and possible replenishment mechanisms by internal or external sources; isotopic composition and time evolution of isotopic ratios; winds and dynamics; condensates and meteorology; and the chemical composition of large particulates (haze particles). All of these topics have been covered extensively in reviews and chapters elsewhere,[7,20,21] and in two books written about the results of the *Cassini*−*Huygens* mission.[22,23]

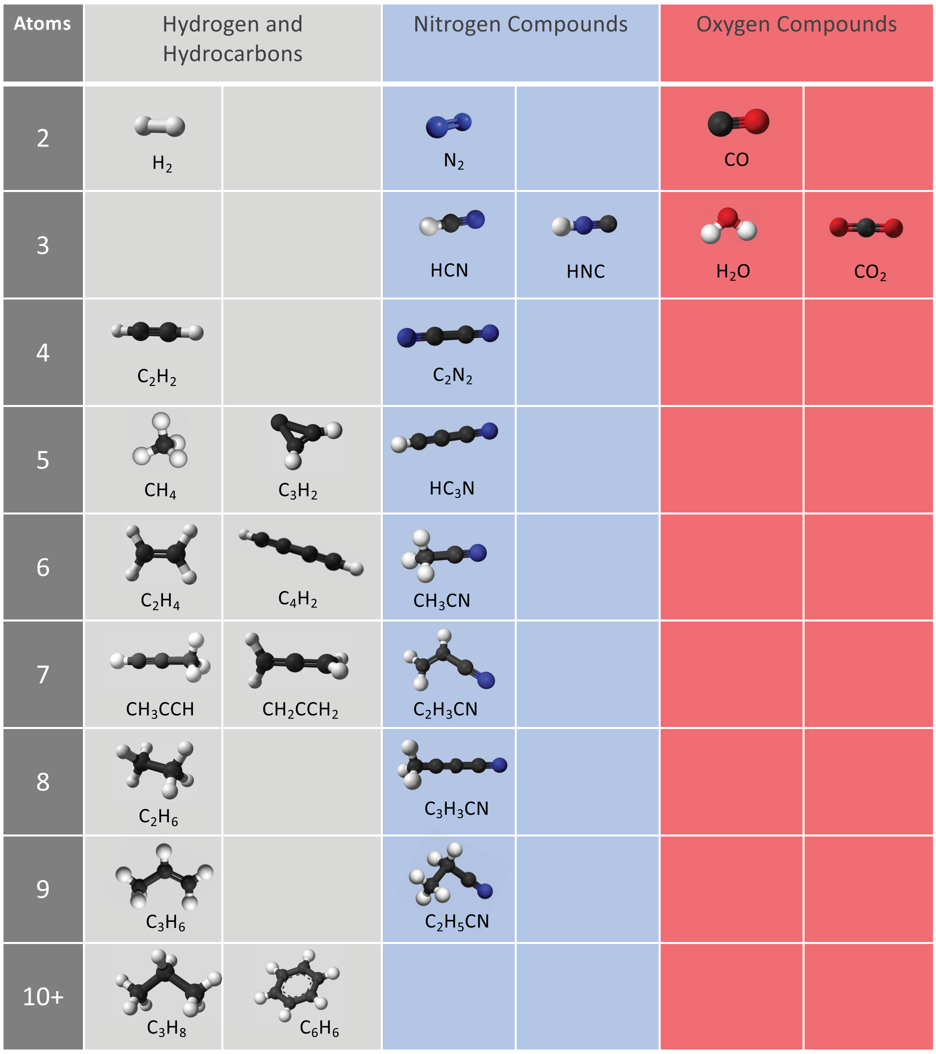

Figure 3. Molecules detected in Titan's neutral atmosphere sorted by number of atoms and composition. Hydrocarbons are the most abundant and complex species type, followed by nitriles. No complex oxygen-bearing molecules, including organics, have been detected on Titan to date.

In presenting an overview and summary focusing on the chemistry and composition of the neutral atmosphere, it is hoped that I will do sufficient justice to this one area to make this review a useful primer for undergraduate or graduate students or others new to the field, to quickly gain a basic understanding of Titan's bulk atmospheric composition and why it is that way—at least at the present era.

The review is organized as follows: I first review basic knowledge about Titan's atmospheric temperature structure and gas composition. The main section of the review contains an exposition on the chemistry of the 24 known molecules in the neutral lower atmosphere. This is followed by a detailed discussion of future research directions in Titan atmospheric composition studies, followed by a Summary and Conclusions.

■ ATMOSPHERIC COMPOSITION AND STRUCTURE

Atmospheric Composition. Titan's atmosphere is largely composed of two gases: N_2 and CH_4. The vertical profile of methane comes from measurements by instruments on the *Cassini–Huygens* space mission, primarily the *Huygens* Gas Chromatograph and Mass Spectrometer (GCMS)[24] from 0–146 km, the *Cassini* Visual and Infrared Mapping Spectrometer (VIMS)[25] (50–850 km), the *Cassini* Ultraviolet Imaging Spectrometer (UVIS)[26] (400–1650 km), and the *Cassini* Ion and Neutral Mass Spectrometer (INMS)[27] (900–1500 km). Their results have been reported in publications from the mission.[28−31]

Aside from noble gases (^{36}Ar, ^{40}Ar, and ^{22}Ne),[31,32] 22 molecular species other than N_2 and CH_4 have been definitively detected in Titan's atmosphere at the time of writing (see Figure 3): 10 hydrocarbons (C_2H_2, C_2H_4, C_2H_6, c-C_3H_2, CH_2CCH_2, CH_3CCH, C_3H_6, C_3H_8, C_4H_2, and c-C_6H_6), eight cyanides[1] (HCN, HNC, HC_3N, C_2N_2, CH_3CN, C_2H_3CN, C_2H_5CN, and CH_3C_3N), three oxygen-bearing species (CO, CO_2, and H_2O), and H_2. These gases were originally detected by a variety of astronomical and remote sensing techniques from the ground and space.

All of the major types of hydrocarbons have been detected (alkanes, alkenes, alkynes, a carbene, and an aromatic ring). However, major chemical families of nitrogen-bearing molecules (including amines, imines, azines, and N-heterocyclic rings) and oxygen-bearing molecules (such as aldehydes, ketones, alcohols, and ethers) are possible ingredients of the atmosphere but remain undetected—a subject we will return to in a later section.

Oxygen has yet to be detected on Titan in an organic molecule such as methanol (CH_3OH) or formaldehyde (H_2CO), being

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found so far only in the simple inorganic molecules CO, CO_2, and H_2O. This limits the presently confirmed scope of astrobiological molecules (i.e., those with the elements CHON in a variety of functional groups), at least in the atmosphere. At the surface and in the subsurface, where hydrocarbons are thought to be readily hydrolyzed as seen in laboratory experiments,[33−35] the astrobiological potential may be much greater.[36−38]

The reaction pathways that lead between these molecules have been compiled into computational models of the atmospheric chemistry, which have largely been successful at replicating the observed gas abundances. Models predating the *Cassini*−*Huygens* mission[39−47] primarily focused on replicating the observed neutral gas abundances as measured by *Voyager*[48] and the *Infrared Space Observatory* (ISO).[49] However, some models were also developed for the ionosphere.[50−54] During the *Cassini*−*Huygens* mission and since, new information collected by the spacecraft, especially from direct sampling of the ionosphere,[28,55−78] has prompted many new and revised models of Titan's atmosphere.[79−103]

At the opposite end of the size scale, molecular growth by covalent bonding and agglomeration results in macromolecular haze particles,[11,61,104−112] composed of thousands to millions of individual atoms.[113] As these particles reach a size of ∼1 μm, they begin to sediment (or form the nuclei for condensate growth) and are removed from the atmosphere,[114−117] apparently forming vast dune fields on the surface.[118−120]

Atmospheric Temperature Structure. Titan's atmospheric temperature structure (Figure 4) is a result of the competing heating and cooling processes that take precedence at different altitudes. In the dense lower atmosphere, convection driven by surface heating leads to a vertically decreasing temperature profile, as warm air rises and adiabatically cools. A temperature minimum is reached at ∼45 km, the tropopause, as confirmed by direct measurements[121] from the *Huygens* Atmospheric Structure Experiment[122] (HASI) and occultations by the *Cassini* Radio Science Subsystem[123] (RSS).[124−126]

Above the tropopause, heating by absorbed solar energy, primarily by atmospheric haze particles, causes temperatures to rise again in the stratosphere.[129] Stratospheric temperatures have been measured by HASI,[121] the *Cassini* Composite Infrared Spectrometer[130] (CIRS),[131,132] and the *Atacama Large Millimeter/submillimeter Array* (ALMA)[128,133,134] as well as through radio occultations for the lower stratosphere.[124−126] At around 250−400 km, a temperature maximum, the stratopause, is reached at ∼180 K.[135] The exact altitude (pressure) and temperature of the stratopause vary with both latitude and season[127,136,137] over the course of Titan's long year (29.46 Earth years), being higher and warmer (by ∼20 K) over the winter pole. This somewhat counterintuitive result can be understood as resulting from adiabatic compression of air in the descending branch of the global stratospheric Hadley cell.

Temperatures fall throughout the next layer, the mesosphere, as haze becomes thin, and radiative cooling by gases such as HCN and C_2H_2 becomes increasingly important.[129,135] Titan's mesopause is reached at ∼600 km,[128] above which altitude temperatures rise again. This is primarily due to methane UV absorption,[138] blocking of outgoing IR radiation by C_2H_6, and far-infrared HCN rotational lines.[129] This is the thermosphere, a region where gas collisions are rare and molecules must wait to spontaneously emit a photon to lose energy.

The temperature structure of the upper atmosphere is highly variable.[52] Thermal oscillations of significant amplitude were inferred by HASI[121] above 500 km, while in situ measurements of electron temperature by the *Cassini* Radio and Plasma Wave Spectrometer (RPWS)[139] and density and composition by INMS have shown significant time variability on diurnal[66,140,141] and longer time scales depending on the level of solar activity[142] as well as the position of Titan within Saturn's magnetosphere.[143−146] More recently ALMA measurements are now able to probe the thermal structure of the upper atmosphere as well, providing the ability to monitor secular changes over time.[128,147]

Above the four layers of the bound atmosphere is the exosphere, beginning at the exobase (∼1500 km[148]), a region where gases can freely escape to space. These five regions mirror the temperature structure of the Earth's atmosphere, but with a substantially larger scale height (approximately ×5) due to the lower surface gravity. Overlapping the upper thermosphere is the ionosphere (z > ∼1000 km), defined as the region where "significant numbers of free thermal (<1 eV) electrons and ions are present".[149]

It is important to note that the vertical profiles of temperature, minor gas abundances, and haze density all vary with both latitude and season. Titan—like Earth and other planets with atmospheres—exhibits one or more convection cells in the middle atmosphere. Near the equinoxes, air rises at midlatitudes and flows to both poles, where it descends and then returns equatorward.[150−154] However, close to the solstices the circulation more closely resembles a single cell with flow from the summer to winter hemisphere. These cells act to redistribute thermal energy, trace gases, and hazes in both altitude and latitude. This topic has been the subject of extensive

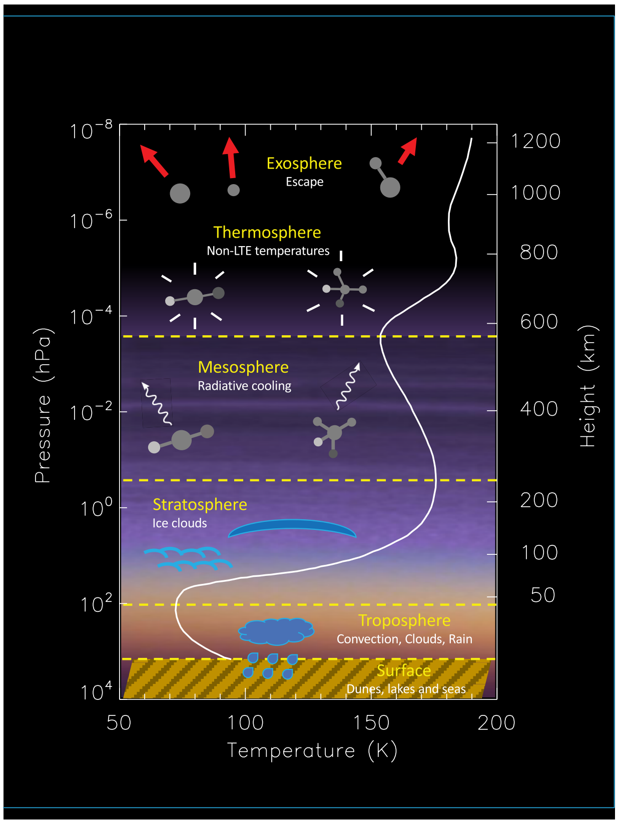

Figure 4. Typical low-latitude atmospheric temperature structure of Titan, composited from multiple measurement sources,[121,124,127,128] showing processes responsible for creating each layer.

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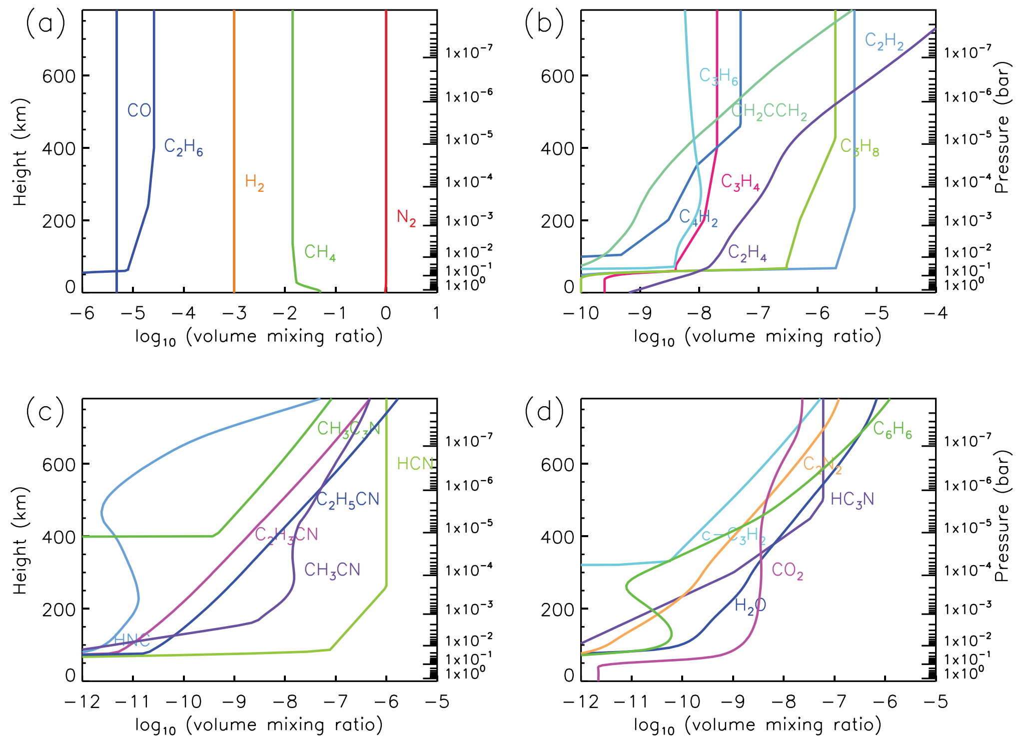

Figure 5. Typical vertical profiles of gases in Titan's atmosphere at low latitudes. Sources: N_2, CH_4, H_2—Niemann et al. (2010);[31] CO—Serigano et al. (2016);[133] C_2H_2, HCN—Teanby et al. (2007);[162] C_2H_6, CH_3CCH, C_3H_8, C_4H_2—Vinatier et al. (2007);[163] HC_3N—Marten et al. (2002);[164] H_2O, C_2N_2—Loison et al. (2015);[98] c-C_3H_2—Nixon et al. (2020);[165] C_2H_3CN—Palmer et al. (2017);[166] C_2H_5CN—Cordiner et al. (2015);[167] CH_3C_3N—Thelen et al. (2020);[168] CH_3CN—2015 profile from Thelen et al. (2019)[169] with extensions to the troposphere from Marten et al. (2002)[164] and the mesosphere from Loison et al. (2015);[98] C_3H_6—Lombardo et al. (2019);[170] CH_2CCH_2—Lombardo et al. (2019);[171] HNC—combination of Lellouch et al. (2019)[128] and Dobrijevic et al. (2016);[101] C_2H_4, c-C_6H_6, CO_2—photochemical models from Vuitton et al. (2019).[103]

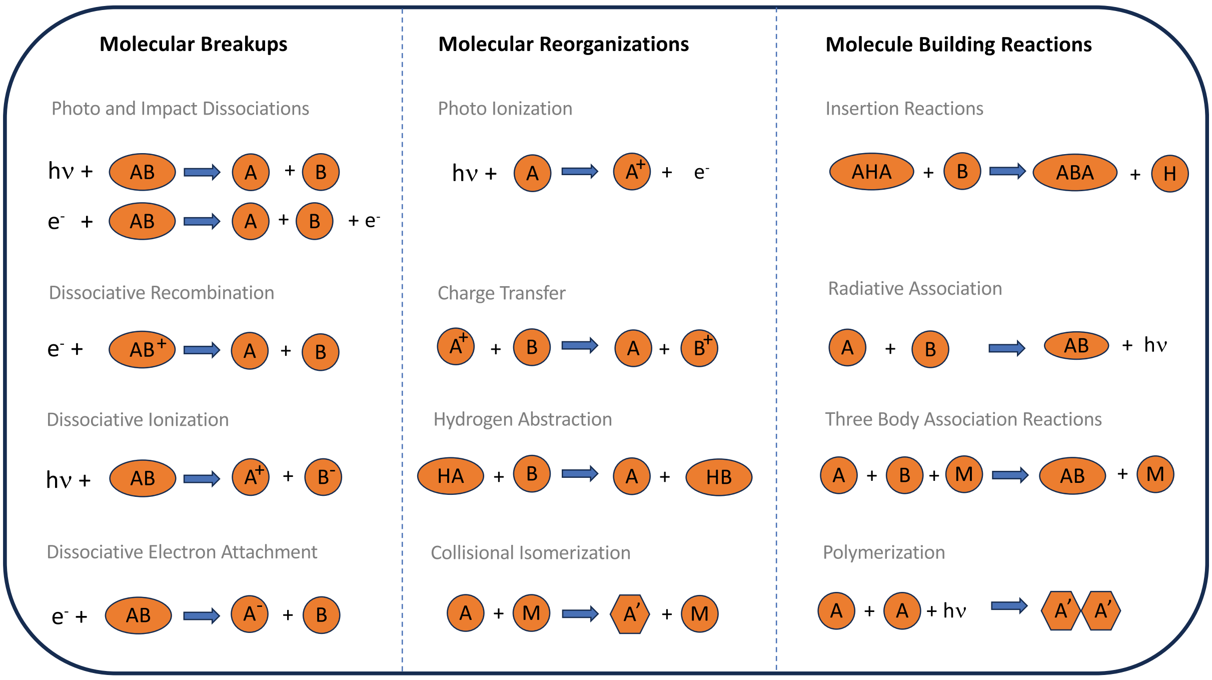

Figure 6. Principal processes and reaction types relevant to the chemistry in Titan's atmosphere. Plus (+) and minus (−) superscripts indicate ions, while A and A′ are molecules that have rearranged into a different structure without change of composition.

measurements and modeling in the literature (see, e.g., refs 127 and 155−161 and references therein). In this review I will not further discuss latitudinal or longitudinal variations in atmospheric structure and will focus only on the vertical chemistry variations typical of mean conditions at low latitudes.

Gas Vertical Profiles. Figure 5 shows typical vertical profiles of the 24 known molecular species at low latitudes, compiled

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from a combination of ground- and space-based measurements, and some photochemical model profiles constrained by observations. These include two pairs of structural isomers: HCN/HNC and CH_3CCH/CH_2CCH_2.

Some important trends can be noted. Methane is an unusual outlier, with a greater abundance in the troposphere ($z \leq 45$ km) than above. This is due to the "cold trap" effect, where it reaches saturation as the tropospheric temperature drops with altitude, and therefore, its mixing ratio is reduced as it forms clouds at ∼15−30 km. The gases N_2 and CO are well-mixed, having approximately uniform profiles throughout the atmosphere due to long photochemical lifetimes. Two other gases, H_2 and C_2H_4, also do not condense at the "cold trap", the coldest part of the atmosphere around the tropopause at 45 km (∼70 K). The profile of H_2 is shown here as constant at the 0.1% value typical of the lower stratosphere, since measurements of its vertical profile remain uncertain.

All other gas species show profiles that typically decrease downward from the upper atmosphere because they have a source due to photochemistry at high altitudes and then become diluted as they are mixed downward into the denser part of the atmosphere. In many cases the actual measured profiles are still rudimentary, constrained by only a few data points and with even less knowledge of meridional and temporal variations. Some gases may exhibit increases again toward the stratosphere due to either secondary production peaks (e.g., due to cosmic ray deposition) or redistribution by atmospheric circulation.

■ ATMOSPHERIC PHOTOCHEMICAL PROCESSES

In this section I present a brief overview of the types of reactions that occur in Titan's atmosphere as a prelude to the discussion of the chemistry of individual molecules in the following section (see also Table 5 of Vuitton et al.[103] and the description therein). Different chemical processes become important at different levels of the atmosphere due to the altitude variation of temperature, density, and penetration depths of charged particles and photons that affect the reactions. For example, Saturn magnetospheric electrons are stopped high up in the ionosphere, while solar photons penetrate to varying depths depending on wavelength.[103] High-energy cosmic rays are deep-penetrating rays in the atmosphere, peaking in energy deposition at around 100−150 km altitude.[103] The various processes, depicted in Figure 6, are now examined in more detail.

Photodissociation and Electron Impact Dissociation. Dissociation (breakup or fragmentation) of a molecule occurs when a sudden influx of energy breaks molecular bonds. In Titan's atmosphere this happens readily in the upper atmosphere ($z >$ ∼700 km) due to both energetic UV solar photons ($h\nu$) and impact of fast-moving electrons (e^-) trapped in Saturn's magnetic field[172,173] (Figure 2).

Dissociation often leads to neutral (uncharged) molecular fragments, which may be in either the ground state or excited states, e.g.:[174−176]

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2 \quad (1)$$

$$CH_4 + e^- \rightarrow {}^3CH_2 + 2H \quad (2)$$

where $^3CH_2$ is ground-state methylene and $^1CH_2$ is an excited state. Note that other possible fragmentation products are possible—the examples given above are only one possibility in each case. Also note that for simplicity, electronic states of molecules are usually omitted in this paper unless they are required to distinguish between two otherwise identical reagents that have significantly different properties.

The molecular fragments are often radicals, i.e., highly reactive atomic or molecular species that have unpaired electrons, such as H, CH, and N. These radicals are quick to react with other radicals or with neutral species.

A secondary peak of dissociation is expected to occur in the deep atmosphere at ∼100−150 km[177−180] due to extremely high energy cosmic rays ($h\nu$).

Ionization. Instead of breaking up (dissociation), a molecule may instead become ionized (positively or negatively charged), typically by losing an electron to become a cation, e.g.:[29,181,182]

$$N_2 + h\nu \rightarrow N_2^+ + e^- \quad (3)$$

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \quad (4)$$

However, dissociative ionization may also occur, e.g.:[183,184]

$$CH_4 + h\nu \rightarrow CH_3^+ + H^- \quad (5)$$

$$C_2H_2 + h\nu \rightarrow H^+ + C_2H^- \quad (6)$$

Ionization of neutrals may also occur through dissociative electron attachment, e.g.:[185,186]

$$CH_4 + e^- \rightarrow CH_2^- + H_2 \quad (7)$$

$$CO + e^- \rightarrow O^- + C \quad (8)$$

For larger molecules, radiative electron attachment is also important:[93,187]

$$C_6H + e^- \rightarrow C_6H^- + h\nu \quad (9)$$

Ion Reactions. Dissociative recombination is the process whereby a positive ion reunites with an electron and in the process breaks apart. An example in Titan's atmosphere is[188,189]

$$CH_5^+ + e^- \rightarrow CH_3 + 2H \quad (10)$$

Radiative association is a reaction whereby two species combine, shedding excess energy via a photon. These reactions typically occur only in rarefied environments ($p < 10^{-5}$ mbar[190]), where a metastable intermediary complex has time to form and then stabilize by emission of a photon. Despite being impossible to observe in laboratory conditions due to the long lifetimes of the intermediate states,[191,192] such reactions are thought to occur in interstellar clouds[193−196] as well as in Titan's upper atmosphere. Radiative ion−neutral association reactions on Titan may include:[103,197]

$$C_4H_3^+ + C_2H_2 \rightarrow C_6H_5^+ + h\nu \quad (11)$$

$$C_3H_3^+ + H_2 \rightarrow C_3H_5^+ + h\nu \quad (12)$$

In charge transfer reactions,[103,198] at least two products result:

$$CH_4^+ + HCN \rightarrow HCNH^+ + CH_3 \quad (13)$$

$$N^+ + C_2H_2 \rightarrow C_2H_2^+ + N \quad (14)$$

Ions may also react with each other, leading to neutral products, although Vuitton et al.[103] argued that positive−negative ion recombination rates are too low to compete with ion−neutral reaction pathways.

Radical Reactions. Radicals (molecules with an unpaired electron) react with other radical and nonradical species in multiple ways. Radicals may react with each other in association reactions:[47]

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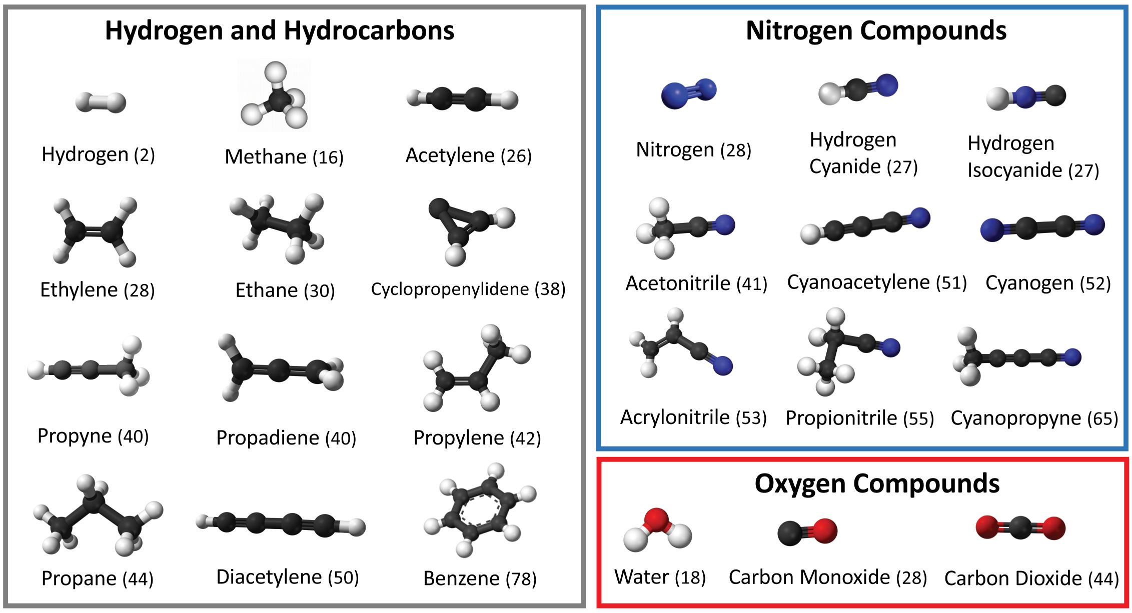

Figure 7. Molecules detected in Titan's neutral atmosphere, along with the mass of the most abundant isotopologue in Da.

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \quad (15)$$

Radicals may attack neutral molecules, for example in the case of hydrogen abstraction, which is a major loss process for methane:[41,103,199,200]

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \quad (16)$$

Other examples include substitutions of terminal atoms or groups, typically at carbon−carbon double or triple bonds:[201−203]

$$CN + C_2H_2 \rightarrow HC_3N + H \quad (17)$$

$$CN + C_2H_4 \rightarrow C_2H_3CN + H \quad (18)$$

and insertions, which allow heavier molecules to be built from simpler ones:[204−206]

$$CH + C_2H_4 \rightarrow CH_3CCH + H \quad (19)$$

Three-body association reactions occur when two reactants meet to form a metastable intermediate complex that is then stabilized by collision with a third, nonreacting body that carries away energy, allowing the metastable complex to stabilize. The two steps are

$$A + B \rightarrow AB^* \quad (20)$$

$$AB^* + M \rightarrow AB + M^* \quad (21)$$

where the asterisk is used to denote an excited state. In this paper I typically simplify such reactions to a single step:

$$A + B + M \rightarrow AB + M^* \quad (22)$$

Such reactions are of critical importance to the formation of many hydrocarbons, especially alkanes, e.g.:[197,207,208]

$$CH_3 + H + M \rightarrow CH_4 + M^* \quad (23)$$

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M^* \quad (24)$$

Note that three-body reactions are limited to Titan's dense lower atmosphere, where there is a sufficiently high collision rate to allow the collisional stabilization to occur.[94]

Radiative association reactions may also occur between radicals. Vuitton et al.[94] studied the effect of radiative associations on Titan's chemistry and proposed that reactions such as

$$C_4H_2 + H \rightarrow C_4H_3 + h\nu \quad (25)$$

and

$$C_4H_3 + H \rightarrow C_4H_4 + h\nu \quad (26)$$

may occur in Titan's atmosphere.

Other Reactions. Molecules may also reorganize their structure to become more stable, such as in collisional isomerization. Two important known instances of this on Titan are the conversion of propadiene (allene) to propyne by H atoms,[41,99] with a barrier of 65.1 kcal/mol:[209]

$$CH_2CCH_2 + H \rightarrow CH_3CCH + H \quad (27)$$

and conversion of HNC to HCN[100] with a barrier of 30.2 kcal/mol:[210]

$$HCN + H \rightarrow HNC + H \quad (28)$$

Polymerization is the process where multiple similar unsaturated hydrocarbons join together form linear chains:

$$nC_2H_4 + h\nu \rightarrow CH_3(C_2H_4)_{n-2}CH_3 + C_2H_2 \quad (29)$$

Polymerization is thought to be one of the principal mechanisms leading to the formation of larger polyyne compounds, which may be a significant component of Titan's haze particles.[80,104,106,108,116,211−218]

CHEMISTRY OF THE NEUTRAL ATMOSPHERE

In this review, I focus on the 24 molecules detected in Titan's dense neutral atmosphere (Figure 7). Many other neutral species have been inferred from ion and neutral mass spectroscopy in Titan's upper atmosphere[28,58,61,65,219,220] through photochemical models[79−88,90−103] and via laboratory experiments (see the review by Cable et al.[111]). The choice to limit the discussion to the chemistry and composition of the 24 definitively identified molecules of the neutral atmosphere was

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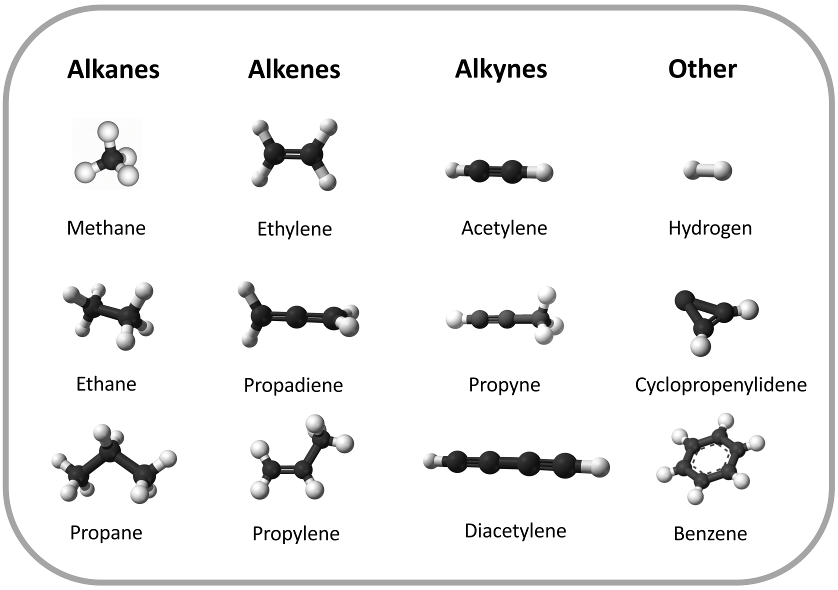

Figure 8. Hydrocarbon molecules detected on Titan.

made for several reasons: (i) this set of molecules includes the most easily detectable and likely the most abundant molecules of the atmosphere, which therefore provide a good overview of bulk chemistry and composition; (ii) other molecules inferred only through single-stage mass spectrometry do not have robust structural identifications, since this technique cannot typically distinguish between isomers having the same chemical formula occurring at the level of complexity of three carbon atoms and beyond; (iii) to allow for a more detailed discussion of the molecules that have been unambiguously detected; and (iv) because the composition of the neutral lower atmosphere is the most important chemical inventory for consideration of other processes such as condensation and meteorology, sedimentation to the surface, and astrobiology at Titan's surface and interior.

Note on Chemical Names. The topic of chemical nomenclature remains eternally problematic. For example, the relatively simple compound C_2H_3CN has been commonly referred to as "vinyl cyanide" in most 20th century astronomical literature, though preference has shifted more recently toward the simpler single-word name "acrylonitrile" (also with "methyl cyanide" to "acetonitrile"). In fact, multiple valid names for C_2H_3CN exist, including "2-propenenitrile", "cyanoethene/cyanoethylene", and "propenenitrile"; however, it must be noted that the preferred official (IUPAC) name is actually the rather cumbersome "prop-2-enenitrile".

IUPAC molecular nomenclature certainly has its place. However, for the purposes of discourse in planetary atmospheric chemistry, dominated by small molecules, the formulaic names for molecules can be not only inconvenient but also an actual obstacle to reading and digesting information. Therefore, in this work I have followed a naming convention based on a combination of modernity modified in places for greater simplicity: (a) single-word names are generally preferred over multiple-word names (e.g., "propyne" over the older standard "methyl acetylene"); (b) numbers in names of small molecules are avoided except where necessary, and (c) it is accepted that some names are close enough to be interchangeable (e.g., there is little confusion engendered by using either "ethylene" or "ethene", "propylene" or "propene", etc.).

While I run the risk of offending practicing chemists, I hope that the terminology is consistent enough for readers to understand what molecule is being referred to and convenient enough for simplified writing in typical planetary science usage.

Hydrocarbons and Hydrogen. Hydrocarbons are molecules formed from atoms of only hydrogen and carbon. Due to the fourfold valency of carbon, many bonding configurations are possible. The most common families of aliphatic (acyclic) hydrocarbons include (i) the alkanes, where carbon is saturated, having four single bonds, and the two unsaturated types: (ii) alkenes, featuring carbon−carbon double bonds, and (iii) alkynes with carbon−carbon triple bonds. Once there are three or more carbon atoms, mixed types become possible (see Figure 8).

Cyclic hydrocarbons occur where there are one or more closed rings of carbon atoms (at least three are needed to make a ring, or cycle). Cyclic molecules that have delocalized π bonding electrons are known as "aromatic" (small aromatics are typically volatile at room temperature), although not all rings are aromatic. For example the unsaturated six-carbon ring benzene ($c\text{-}C_6H_6$) is a well-known aromatic, whereas its saturated cousin cyclohexane ($c\text{-}C_6H_{12}$) is a nonaromatic cycle. Carbenes are reactive molecules where carbon has two unbonded but paired electrons, such as methylene (CH_2).

Hydrocarbon molecules are created through the breakup and recombination of fragments of methane. A prime example is the formation of ethane from two methyl radicals:[221,222]

$$CH_4 + h\nu \rightarrow CH_3 + H \tag{30}$$

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M^* \tag{31}$$

Note that in the process, significant amounts of molecular hydrogen will form from the photodissociated hydrogen atoms:[223]

$$2H + M \rightarrow H_2 + M^* \tag{32}$$

leading to the trace amounts of hydrogen (~0.1%) found in Titan's lower atmosphere. Note that this termolecular reaction is an important process leading to the creation of H_2 in the interstellar medium (ISM).

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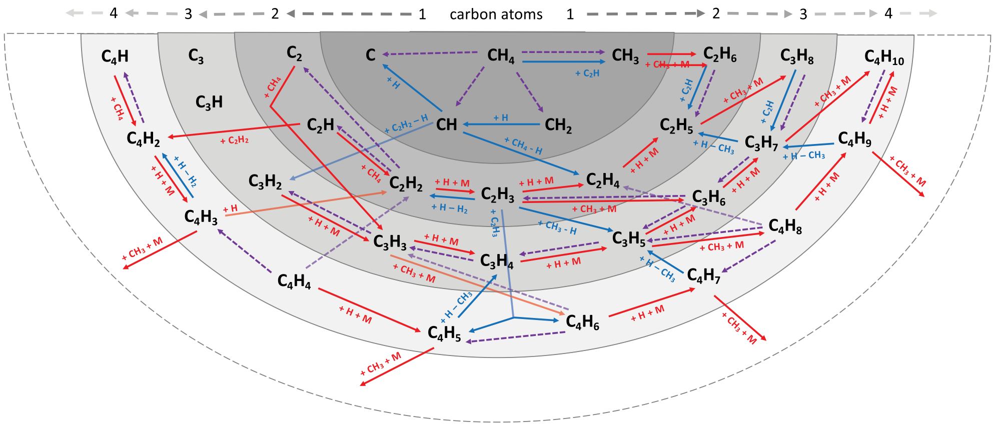

Figure 9. Hydrocarbon chemical reagent and reaction networks showing key pathways. Photolysis pathways are shown in purple dashed lines, three-body reactions in red, and other reactions in blue. As the number of carbon atoms increases, the number of possible species multiplies.

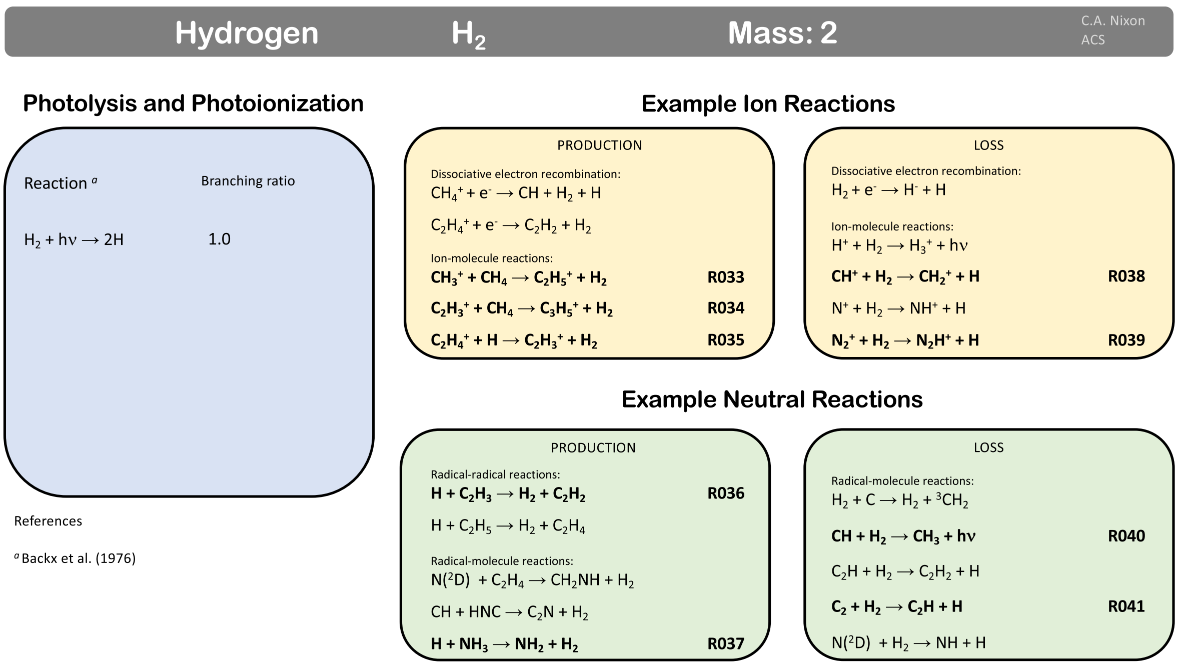

Figure 10. Hydrogen production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Significant loss of hydrogen to space is thought to occur,[40,148,224−228] preventing methane from being recycled, as occurs on the giant planets, leading to gradual depletion of methane in Titan's atmosphere in the absence of outgassing or other replenishment.[41,229−232]

A network diagram showing the principal neutral pathways for hydrocarbon molecule formation is shown in Figure 9. Hereafter follows a high-level description of the key chemistry for each of the hydrocarbons and hydrogen leading to their relative abundances in the neutral atmosphere.

Hydrogen. Detection. Molecular hydrogen (H_2) was was tentatively detected by Trafton[233] using the 107 inch telescope at the McDonald Observatory via absorption in the S(0) and S(1) quadrupole lines of the 3−0 band at ∼0.82 μm. Hydrogen was clearly detected in the far-infrared by the *Voyager* 1 Infrared Interferometer Spectrometer (IRIS)[234] and confirmed by *Cassini* CIRS.[235] The H_2 volume mixing ratio (VMR) was measured directly by the *Cassini* INMS instrument in the ionosphere at 0.4%[28] and in the lower stratosphere and troposphere by *Huygens* GCMS at 0.1%.[31] The fact that hydrogen, presumed to be produced in the upper atmosphere by photolysis of methane,[40,41] was measured to have a decreasing abundance downward, has proved difficult to replicate in models. Models have required a sink for H_2 at the surface,[135,225,236] which has even been suggested as possibly biological in origin.[237] Important reactions for hydrogen are shown in Figure 10.[238]

Production. Molecular hydrogen can be produced in ion-phase reactions, such as[239]

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (33)$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \quad (34)$$

$$C_2H_4^+ + H \rightarrow C_2H_3^+ + H_2 \quad (35)$$

and in neutral-phase radical reactions, including[103,240]

$$H + C_2H_3 \rightarrow C_2H_2 + H_2 \quad (36)$$

$$H + NH_3 \rightarrow NH_2 + H_2 \quad (37)$$

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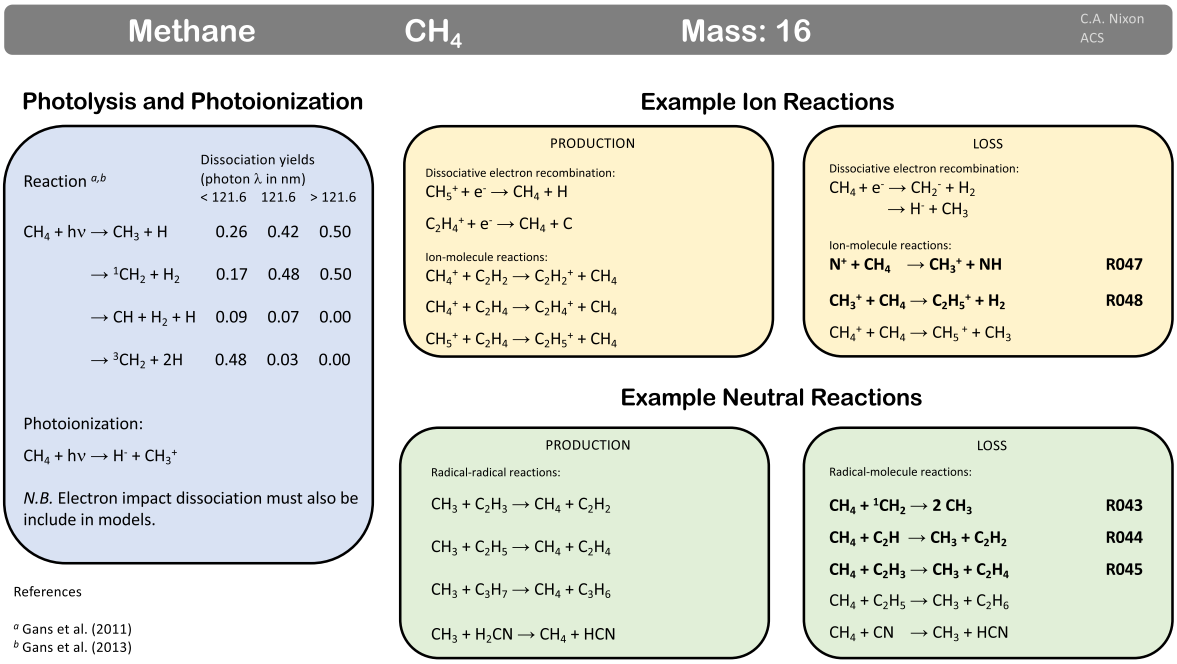

Figure 11. Methane production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Loss. H_2 may be lost to photolysis, yielding two H atoms, although Vuitton et al.[103] have argued that this is a relatively small source of H in Titan's atmosphere due to shielding of H_2 by CH_4 and N_2, with most H production coming from photolysis of methane.

H_2 may also be lost due to ion reactions, e.g.,[239,241,242]

$$CH^+ + H_2 \rightarrow CH_2^+ + H \quad (38)$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \quad (39)$$

and radical reactions:[243−245]

$$CH + H_2 \rightarrow CH_3 + h\nu \quad (40)$$

$$C_2 + H_2 \rightarrow C_2H + H \quad (41)$$

Future Work. Measurement and modeling work is still required to confirm our understanding of the vertical H_2 profile[21,135,225] and determine whether a solution to the vertical gradient lies in instrumental errors[228] or unknown processes in the atmosphere.

Methane. Profile. Methane (CH_4) was the first molecule to be positively identified in Titan's atmosphere, via visible and near-IR absorptions seen by Kuiper[246] using the 82 inch reflector at McDonald Observatory. We now know that methane is the basic ingredient enabling all of Titan's complex organic (i.e., carbon) chemistry, allowing reactions to proceed up to the creation of haze particles. Some key reactions for methane are shown in Figure 11.[247,248]

Nevertheless, methane may be a gradually depleting resource since it is not permanently recycled, unless it is replenished by an as yet unidentified mechanism.[41,231,232,249,250] Speculative mechanisms include crustal destabilization leading to outgassing from methane clathrates,[251] outgassing from cryovolcanism,[252−254] and displacement from near-surface clathrate materials by condensed ethane,[255] yet observational evidence for these processes remains inconclusive at best.

Methane's vertical profile can be divided into three zones: (i) a tropospheric zone where the fractional abundance gradually decreases from 5.5% at the surface to a minimum at the tropopause of around 1.4%, due to reaching saturation at decreasing VMRs as the temperature decreases toward the tropopause ("cold trap"); (ii) a relatively constant amount of 1.4% in the stratosphere, mesosphere, and thermosphere; and (iii) a gradually increasing mixing fraction above an altitude of 800−850 km (the methane homopause) in the increasingly collisionless regime, due to the differing scale heights of different molecules.[135] It is presently uncertain whether methane has any variation with latitude on Titan, although a variation from ∼1.0% to 1.5% in the lower stratosphere has been reported[256] based on infrared measurements by *Cassini* CIRS.[256]

Loss. The photolysis of methane in the upper atmosphere leads to the formation of radicals, including methyl (CH_3), methylidene (CH), and the carbene methylene ($^1CH_2$ or $^3CH_2$),[103] which undergo a chain of reactions to form all the hydrocarbons found in Titan's atmosphere. Note that as much as 75% of methane photolysis above 700 km is due to the solar Lyman-α line at 121.6 nm.[257]

The fate of most methane is ultimately to form ethane via the addition of two methyl radicals (reaction 31) or via the creation of ethyl radical,

$$^1CH_2 + CH_4 \rightarrow C_2H_5 + H \quad (42)$$

leading to permanent loss of methane. Methyl radicals are produced either directly by primary photolysis or by reaction of methane with radicals:[205,258]

$$^1CH_2 + CH_4 \rightarrow 2CH_3 \quad (43)$$

$$C_2H + CH_4 \rightarrow CH_3 + C_2H_2 \quad (44)$$

$$C_2H_3 + CH_4 \rightarrow CH_3 + C_2H_4 \quad (45)$$

Note that the reactions of the ethynyl and vinyl radicals (among others) with methane are catalytic destruction processes since the acetylene and ethylene generated are easily photolyzed back to their radical forms, where they can continue to destroy methane molecules. This process may be repeated

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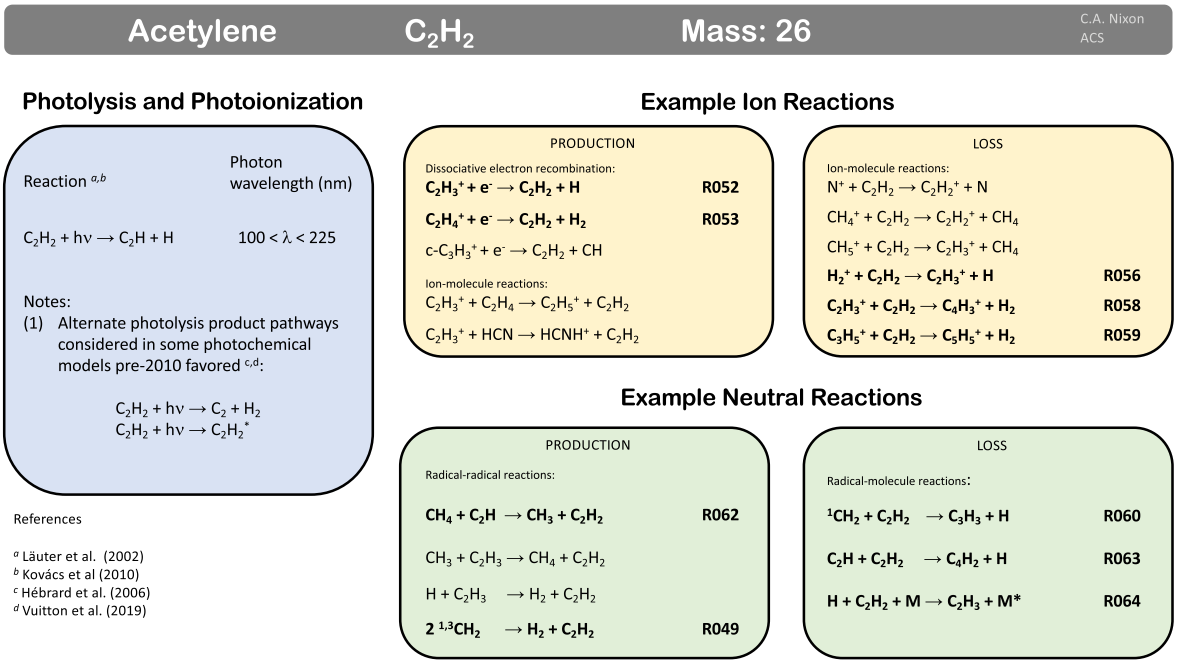

Figure 12. Acetylene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

hundreds of times before the radical catalysts are themselves lost to form higher hydrocarbons. This is the main source of methane depletion in Titan's atmosphere.[103]

Methane fragments participate in ion chemistry. They first are ionized by charge transfer:[242]

$$N_2^+ + CH_3 \rightarrow CH_3^+ + N_2 \quad (46)$$

$$N^+ + CH_4 \rightarrow CH_3^+ + NH \quad (47)$$

Then they build up C_2H_x ions, e.g.:[239]

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (48)$$

Future Directions. Although the chemistry of methane is perhaps one of the best-understood for any molecule on Titan, the most pressing questions remain the nature of its origin and possible replenishment.[21]

Acetylene. Acetylene was the third molecule to be identified in Titan's atmosphere,[259] following the detection of methane and ethane, when Gillett observed its 13 μm band in mid-infrared spectroscopy with 2 and 4 m telescopes at Kitt Peak Observatory. Important reactions for acetylene are shown in Figure 12.[103,257,260,261]

Production. Acetylene may be produced from photolysis products of methane either directly, i.e.,[262]

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2 \quad (49)$$

or indirectly via C_2H_4 and other species from photolysis[263] (see Figure 13):

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \quad (50)$$

$$C_2H_4 + h\nu \rightarrow C_2H_2 + 2H \quad (51)$$

Dissociative electron recombination is another production pathway, e.g.,[264,265]

$$C_2H_3^+ + e^- \rightarrow C_2H_2 + H \quad (52)$$

$$C_2H_4^+ + e^- \rightarrow C_2H_2 + 2H/H_2 \quad (53)$$

Loss. In the ionosphere, photolysis of acetylene and electron transfer to N_2^+ produce $C_2H_2^+$,[242] which reacts with neutrals to build heavier ions,[239] e.g.,

$$C_2H_2^+ + CH_4 \rightarrow C_3H_4^+ + H_2 \quad (54)$$

$$C_2H_2^+ + CH_4 \rightarrow C_3H_5^+ + H \quad (55)$$

which may (dissociatively) recombine with e^- to form neutral C_3H_x species.[266,267] Likewise, proton transfer to neutral acetylene leads to $C_2H_3^+$, which can also form C_3 species:[239]

$$H_2^+ + C_2H_2 \rightarrow C_2H_3^+ + H \quad (56)$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \quad (57)$$

Finally, neutral C_2H_2 in the ionosphere may combine with other ions to build heavier species,[239] e.g.,

$$C_2H_3^+ + C_2H_2 \rightarrow C_4H_3^+ + H_2 \quad (58)$$

$$C_3H_5^+ + C_2H_2 \rightarrow C_5H_5^+ + H_2 \quad (59)$$

In the neutral atmosphere, acetylene is lost by reaction with methylene to form propargyl:[268−270]

$$^1CH_2 + C_2H_2 \rightarrow C_3H_3 + H \quad (60)$$

Acetylene absorbs photons at longer wavelengths (~230 nm[79]) than methane, so its photolysis continues into the stratosphere (see Figure 12). This produces ethynyl (C_2H) and carbyne (C_2), which are potent means of methane depletion via hydrogen abstraction:[223]

$$C_2 + CH_4 \rightarrow C_2H + CH_3 \quad (61)$$

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \quad (62)$$

The acetylene produced by this reaction is recycled back to ethynyl by photolysis, and thereby each acetylene/ethynyl may cause the loss of hundreds of methane molecules before being lost itself to another reaction pathway, such as[271]

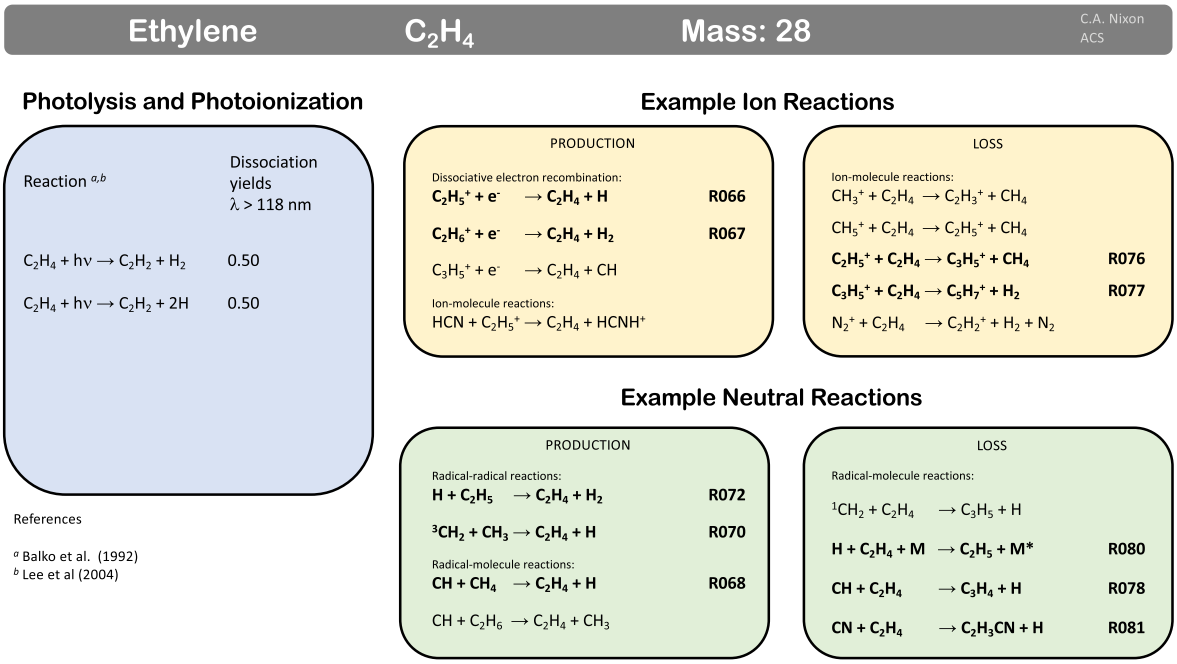

Figure 13. Ethylene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \quad (63)$$

Catalytic destruction of methane in this way is the principal means of methane depletion in Titan's atmosphere.[41,79,103] In the lower atmosphere (z < 500 km), the dominant loss process for acetylene is conversion to ethylene by a two-step reaction with atomic hydrogen:[94,103]

$$C_2H_2 + H + M \rightarrow C_2H_3 + M^* \quad (64)$$

$$C_2H_3 + H + M \rightarrow C_2H_4 + M^* \quad (65)$$

Future Directions. Acetylene has been detected on Titan's surface[32,272] and is likely to be present in the northern lakes and seas.[273,274] Future investigation by the mass spectrometer (DrAMS) instrument of *Dragonfly*[275] will further refine the surface and near-surface abundance.

C_2H_2 was one of the first molecules investigated to form a cocrystal[276,277] at Titan surface temperatures, an organized cocondensate of two or more chemical species. The validity of multiple cocrystal types has since been established, but further laboratory work is required to determine the full parameter space of possible crystalline types.

Ethylene. Ethylene (C_2H_4) was discovered by infrared spectroscopy at the same time as acetylene.[259] The vertical profile of ethylene exhibited a surprising trend to decrease in abundance upward in the lower stratosphere early in the *Cassini* mission,[163,278] although this faded at later seasons.[127,137]

Ethylene is a crucial two-carbon neutral molecule that provides a stepping stone from methane to higher hydrocarbons (Figure 13).[279,280] Ethylene is remarkable in being one of the few molecules (along with CO, H_2, and N_2) that does not condense at the tropopause and therefore persists in significant quantities into the troposphere.

Production. Ethylene may be produced in the ionosphere by dissociative recombination of heavier ions with an electron:[266,281,282]

$$C_2H_5^+ + e^- \rightarrow C_2H_4 + H \quad (66)$$

$$C_2H_6^+ + e^- \rightarrow C_2H_4 + H_2 \quad (67)$$

In the neutral atmosphere, ethylene is largely formed through reactions between methane and its derived radicals or between radicals:[79,257,262,268,269,283]

$$CH + CH_4 \rightarrow C_2H_4 + H \quad (68)$$

$$^1CH_2 + CH_3 \rightarrow C_2H_4 + H \quad (69)$$

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \quad (70)$$

At lower altitudes, production through the C_2H_5 intermediate is also important:[223]

$$^1CH_2 + CH_4 \rightarrow C_2H_5 + H \quad (71)$$

$$H + C_2H_5 \rightarrow C_2H_4 + H_2 \quad (72)$$

Loss. In the ionosphere, the ethylenium ion—produced from ethylene photoionization—can be lost in various reactions with neutrals:[239]

$$C_2H_4^+ + H \rightarrow C_2H_3^+ + H_2 \quad (73)$$

$$C_2H_4^+ + C_2H_2 \rightarrow c\text{-}C_3H_3^+ + CH_3 \quad (74)$$

$$C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3 \quad (75)$$

Also, ethylene can be lost during the formation of heavier ions:[239]

$$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4 \quad (76)$$

$$C_3H_5^+ + C_2H_4 \rightarrow C_5H_7^+ + H_2 \quad (77)$$

Photolysis of ethylene leads to acetylene (reactions 50 and 51). Insertion/addition reactions onto ethylene by CH, for example, can lead to higher hydrocarbons:[204,283,284]

$$C_2H_4 + CH \rightarrow CH_3CCH + H \quad (78)$$

$$C_2H_4 + CH \rightarrow CH_2CCH_2 + H \quad (79)$$

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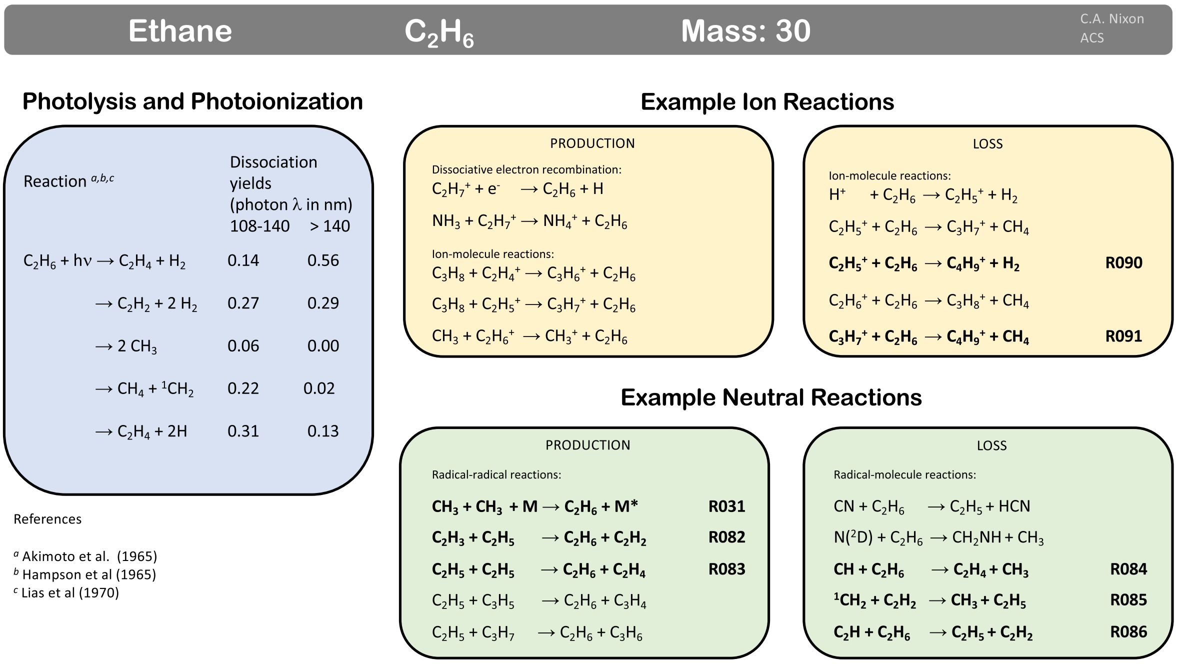

Figure 14. Ethane production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Below 500 km, loss via H addition becomes important:[94]

$$H + C_2H_4 + M \rightarrow C_2H_5 + M^* \tag{80}$$

The CN radical can also substitute onto ethylene to create vinyl cyanide (also known as acrylonitrile or propenitrile):[98,202,203]

$$C_2H_4 + CN \rightarrow C_2H_3CN + H \tag{81}$$

Future Directions. Ethylene is the simplest alkene, the family of hydrocarbons having a C═C double bond. Photolysis or other breaking of the alkene C═C bond leads to radicals which rapidly react, leading to formation of polymers. The role of polymer formation in Titan's atmosphere is incompletely understood but is likely to be an important process in the formation of haze particles.

Ethane. Ethane was the second molecule to be discovered in Titan's atmosphere, via its strong ν_9 band at 12 μm[285] seen by Gillett with the 60 inch telescope on Mount Lemmon. Ethane forms one of the primary trace gases in Titan's atmosphere, with concentrations greater than 1 ppm in the stratosphere,[48,286,287] and is the primary sink for methane loss.[41,47] Due to this observation, a global deep ethane ocean was originally predicted[288,289] but later proved not to be the case.[290,291]

The liquid hydrocarbon bodies eventually detected on Titan's surface[292] have a measured ethane content that varies between different seas and is generally less than the methane fraction,[293,294] except for the southern lake *Ontario Lacus*.[295,296] Ethane may form cocrystals in Titan lakes with other organics, such as benzene.[297] Ethane has also been implicated in displacing methane from clathrate hydrate, allowing for a partial resupply mechanism of methane to the atmosphere,[255] which is otherwise continuously lost by chemistry.[41,298]

Production. Ethane is primarily produced by the addition of two methyl radicals (reaction 31) but also reforms from the ethyl radical:[299]

$$C_2H_3 + C_2H_5 \rightarrow C_2H_6 + C_2H_2 \tag{82}$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4 \tag{83}$$

Ethane is also formed in ion reactions, as shown in Figure 14.[300−302]

Loss. Ethane can be lost through photolysis back to two CH_3 radicals or to stable molecules such as ethylene and acetylene with loss of hydrogen (see Figure 14). Ethane can also be attacked by reactive radicals such as methylidene, methylene, and ethynyl (from acetylene photolysis):[79,204,223,283]

$$CH + C_2H_6 \rightarrow CH_3 + C_2H_4 \tag{84}$$

$$^1CH_2 + C_2H_6 \rightarrow CH_3 + C_2H_5 \tag{85}$$

$$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5 \tag{86}$$

Ethane may form heavier ions through reactions such as[239]

$$C_2H_2^+ + C_2H_6 \rightarrow C_3H_5^+ + CH_3 \tag{87}$$

$$C_2H_2^+ + C_2H_6 \rightarrow C_4H_7^+ + H \tag{88}$$

$$C_2H_3^+ + C_2H_6 \rightarrow C_4H_7^+ + H_2 \tag{89}$$

$$C_2H_5^+ + C_2H_6 \rightarrow C_4H_9^+ + H_2 \tag{90}$$

$$C_3H_7^+ + C_2H_6 \rightarrow C_4H_9^+ + CH_4 \tag{91}$$

Future Directions. Large amounts of ethane are thought to condense in Titan's lower stratosphere and form a significant fraction of Titan's lakes and seas.[273,303] Ethane was implicated in the formation of a vast north polar cloud seen during northern winter in 2005 by *Cassini* VIMS,[304] although other interpretations have suggested that this cloud is condensed methane.[305] While the basic chemistry of ethane is well-understood, an improved understanding of its condensation—especially cocondensation with other gases—will be crucial to a more accurate interpretation of Titan's meteorology.

Cyclopropenylidene. Cyclopropenylidene (c-C_3H_2) is the first carbene (a molecule having two unbonded, self-paired valence electrons from a carbon atom) and the second cyclic

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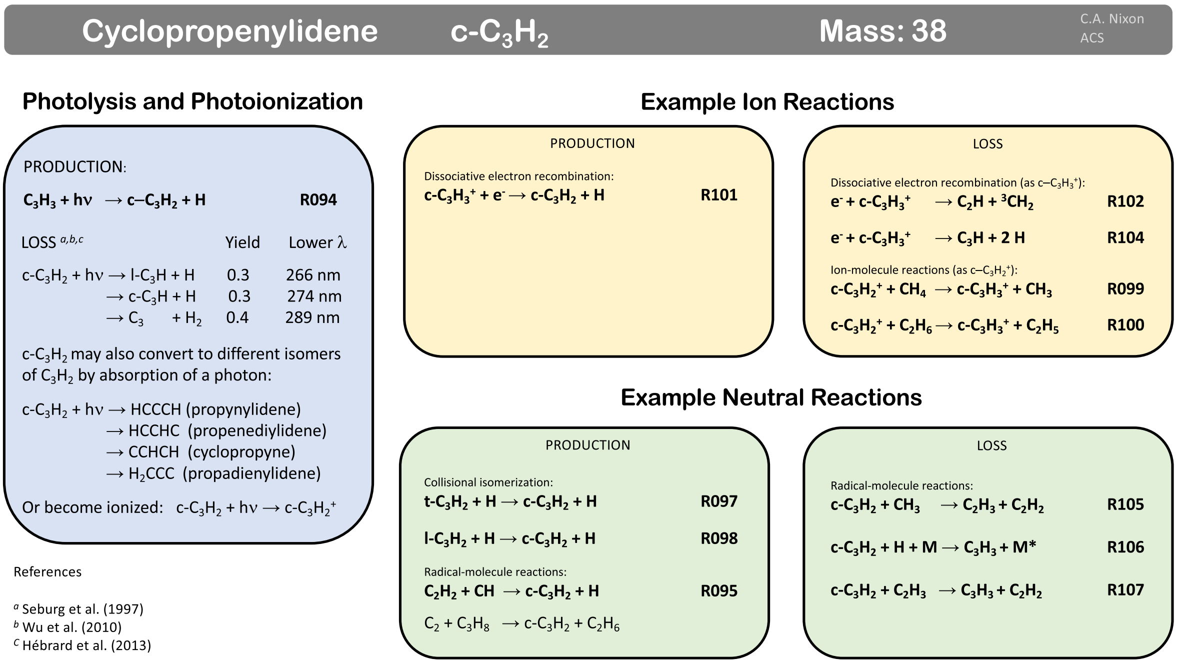

Figure 15. Cyclopropenylidene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

molecule to be found in Titan's atmosphere (after benzene). c-C_3H_2 was detected using millimeter-wavelength astronomy with ALMA,[165] the third molecule whose first detection on Titan was achieved with this telescope.

Production. In the upper atmosphere, production of a precursor, the cyclopropenyl cation (c-$C_3H_3^+$) is thought to proceed by[103]

$$C_2H_5^+ + C_2H_2 \rightarrow \text{c-}C_3H_3^+ + CH_4 \quad (92)$$

$$C_2H_4^+ + C_2H_2 \rightarrow \text{c-}C_3H_3^+ + CH_3 \quad (93)$$

c-$C_3H_3^+$ then recombines with e^- to produce c-C_3H_2[306] and H.

Another possible pathway involves photolysis of propargyl:

$$C_3H_3 + h\nu \rightarrow \text{c-}C_3H_2 + H \quad (94)$$

In the neutral atmosphere, the dominant production pathways may include CH addition to acetylene[307,308] (see Figure 15):[309,310]

$$CH + C_2H_2 \rightarrow \text{c-}C_3H_2 + H \quad (95)$$

Below 600 km, the following reaction can occur:[311]

$$H_2 + \text{c-}C_3H \rightarrow \text{c-}C_3H_2 + H \quad (96)$$

c-C_3H_2 can also result from collisional isomerization from its isomers propynylidene (t-C_3H_2) and propadienylidene (l-C_3H_2):[311]

$$H + \text{t-}C_3H_2 \rightarrow H + \text{c-}C_3H_2 \quad (97)$$

$$H + \text{l-}C_3H_2 \rightarrow H + \text{c-}C_3H_2 \quad (98)$$

Loss. Once ionized, the c-$C_3H_2^+$ ion may abstract hydrogen from neutrals to form the c-$C_3H_3^+$ ion:[239,312]

$$\text{c-}C_3H_2^+ + CH_4 \rightarrow \text{c-}C_3H_3^+ + CH_3 \quad (99)$$

$$\text{c-}C_3H_2^+ + C_2H_6 \rightarrow \text{c-}C_3H_3^+ + C_2H_5 \quad (100)$$

c-$C_3H_3^+$ in turn may dissociatively recombine with an electron, returning to c-C_3H_2, or splinter into smaller acyclic fragments:[266,313]

$$\text{c-}C_3H_3^+ + e^- \rightarrow \text{c-}C_3H_2 + H \quad (101)$$

$$\text{c-}C_3H_3^+ + e^- \rightarrow C_2H + {}^3CH_2 \quad (102)$$

$$\text{c-}C_3H_3^+ + e^- \rightarrow C_2 + CH_3 \quad (103)$$

$$\text{c-}C_3H_3^+ + e^- \rightarrow C_3H + 2H \quad (104)$$

In the neutral atmosphere above 600 km, c-C_3H_2 photodissociates to form c-C_3H, l-C_3H, and C_3. It is also lost by reaction with CH_3 to form acylic species:[311]

$$\text{c-}C_3H_2 + CH_3 \rightarrow C_2H_2 + C_2H_3 \quad (105)$$

Below 600 km, these pathways continue to be significant, but there is additional c-C_3H_2 loss via[311]

$$\text{c-}C_3H_2 + H + M \rightarrow C_3H_3 + M^* \quad (106)$$

$$\text{c-}C_3H_2 + C_2H_3 \rightarrow C_3H_3 + C_2H_2 \quad (107)$$

Future Work. Chemical pathways leading to and from c-C_3H_2 in Titan's atmosphere remain to be explored, especially given the multiple possible structures for C_3H_2, including propynylidene (HC_3H, t-C_3H_2), propadienylidene (H_2CCC, i-C_3H_2), cyclopropyne (CCHCH), and propenediylidene (HCCHC).[309,310] Experimental and theoretical work on reaction pathways, rates, and branching ratios during photolysis will greatly help to clarify the production, loss, and stability of cyclopropenylidene.

Several isomers of C_3H_2 have been detected in space, including H_2CCC,[314] which should prompt further astronomical observations to determine if these isomers also exist in Titan's upper atmosphere. Intriguingly, the CHCCH form has been shown to dimerize to form *p*-benzyne,[307] as discussed in a later section.

Propyne. The propyne (CH_3CCH, methyl acetylene) isomer of C_3H_4 was first detected in the infrared by *Voyager* IRIS[315] via

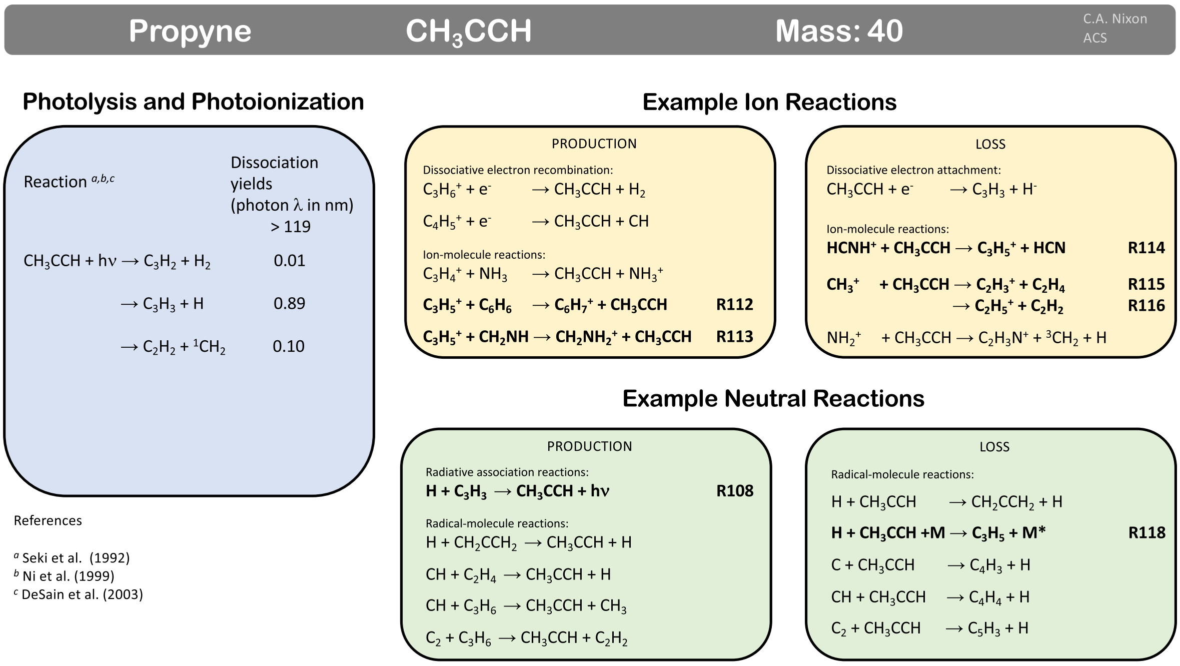

Figure 16. Propyne production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

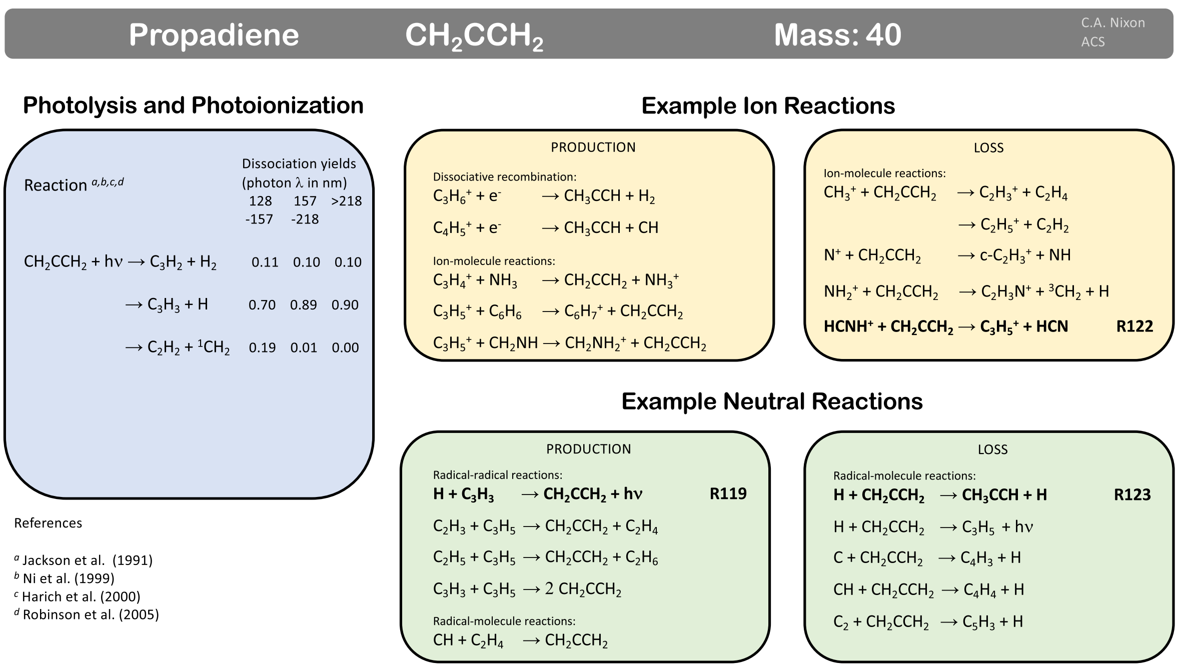

Figure 17. Propadiene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

long-wavelength infrared emission bands at 328 and 633 cm^{-1}.[316]

Production. Propyne and its symmetric isomer propadiene (CH_2CCH_2, allene) are produced by addition of CH into ethylene (reaction 79; see Figure 16)[317−319] but also through H addition to propargyl,[320]

$$H + C_3H_3 \rightarrow CH_3CCH + h\nu \quad (108)$$

or through dissociation of C_3H_6 (see Figure 18):[321]

$$C_3H_6 + h\nu \rightarrow CH_3CCH + 2H \quad (109)$$

In the ionosphere, the $C_3H_5^+$ ion is a precursor to C_3H_4 and is produced via the following reactions:[219]

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \quad (110)$$

$$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4 \quad (111)$$

It then forms C_3H_4 by proton transfer:[322,323]

$$C_3H_5^+ + C_6H_6 \rightarrow C_6H_7^+ + CH_3CCH \quad (112)$$

$$C_3H_5^+ + CH_2NH \rightarrow CH_2NH_2^+ + CH_3CCH \quad (113)$$

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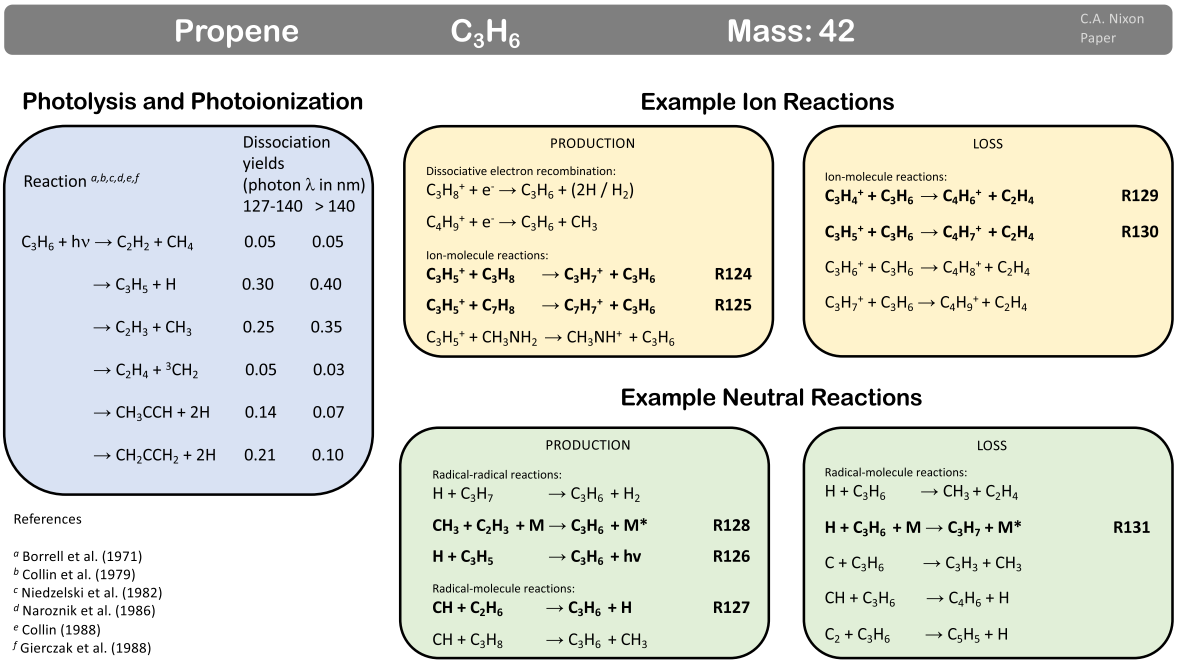

Figure 18. Propene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Loss. In the ionosphere, propyne is lost through ion reactions such as[239]

$$HCNH^+ + CH_3CCH \rightarrow C_3H_5^+ + HCN \quad (114)$$

$$CH_3^+ + CH_3CCH \rightarrow C_2H_3^+ + C_2H_4 \quad (115)$$

$$CH_3^+ + CH_3CCH \rightarrow C_2H_5^+ + C_2H_2 \quad (116)$$

Propyne may also be lost by photolysis in the upper atmosphere[324] and to three-body reactions:[103]

$$CH_3CCH + h\nu \rightarrow C_3H_3 + H \quad (117)$$

$$CH_3CCH + H + M \rightarrow C_3H_5 + M^* \quad (118)$$

Future Work. Many reactions forming or depleting C_3H_4 have uncertain branching ratios between CH_3CCH and its isomer CH_2CCH_2. Further work is needed to improve knowledge of these quantities. Collisional interconversion between the two isomers may be mediated by atomic hydrogen,[99] so accurate measurement of both isomers may be a way to provide a constraint on the abundance of otherwise short-lived and difficult-to-measure H atom.

Propadiene. Propadiene (CH_2CCH_2) is a less abundant and less thermodynamically stable isomer of C_3H_4, which is more abundant in Titan's atmosphere in the form of propyne. Propadiene was detected in Titan's atmosphere using high-resolution ground-based spectroscopy at NASA's Infrared Telescope Facility (IRTF) with the Texas Echelon Cross Echelle Spectrograph (TEXES) instrument via its ν_{10} band at ~845 cm^{-1}.[325]

Production. Like propyne (CH_3CCH), propadiene is produced in the upper atmosphere by CH addition to ethylene (reaction 79; see Figure 17)[318,326−328] and by H addition to C_3H_3:[320]

$$H + C_3H_3 \rightarrow CH_2CCH_2 + h\nu \quad (119)$$

Lower in the atmosphere, where propene is more plentiful, it can be photodissociated to produce propadiene (see Figure 18):[329]

$$C_3H_6 + h\nu \rightarrow CH_2CCH_2 + H_2 \quad (120)$$

Ion formation pathways of CH_2CCH_2 are less certain but may follow similar channels as propyne, with branching ratios that are currently uncertain.

Loss. Propadiene is lost to direct photolysis:[318]

$$CH_2CCH_2 + h\nu \rightarrow C_3H_3 + H \quad (121)$$

It is also lost to ion reactions such as[103]

$$HCNH^+ + CH_2CCH_2 \rightarrow C_3H_5^+ + HCN \quad (122)$$

or by collision with H to form propyne:[103]

$$CH_2CCH_2 + H \rightarrow CH_3C_2H + H \quad (123)$$

Future Directions. As with propyne, the branching ratios of reactions implicated in the formation of C_3H_4 isomers remain uncertain, so further experimental and theoretical work is required. Accurate measurement of both propyne and propadiene is a possible means to indirectly infer the abundance of atomic hydrogen[99] in the lower atmosphere, in the absence of direct in situ measurements.

Propene. Propene (C_3H_6, propylene) was first detected using data from *Cassini* CIRS via its ν_{19} band emission near 11 μm.[171,330]

Production. Ion reactions lead to creation of propene from $C_3H_5^+$, e.g.:[239]

$$C_3H_5^+ + C_3H_8 \rightarrow C_3H_7^+ + C_3H_6 \quad (124)$$

$$C_3H_5^+ + C_7H_8 \rightarrow C_7H_7^+ + C_3H_6 \quad (125)$$

Propene is predicted to be produced in the upper atmosphere by both H addition to C_3H_5 (62%) and CH insertion into ethane (38%):[91]

$$H + C_3H_5 \rightarrow C_3H_6 + h\nu \quad (126)$$

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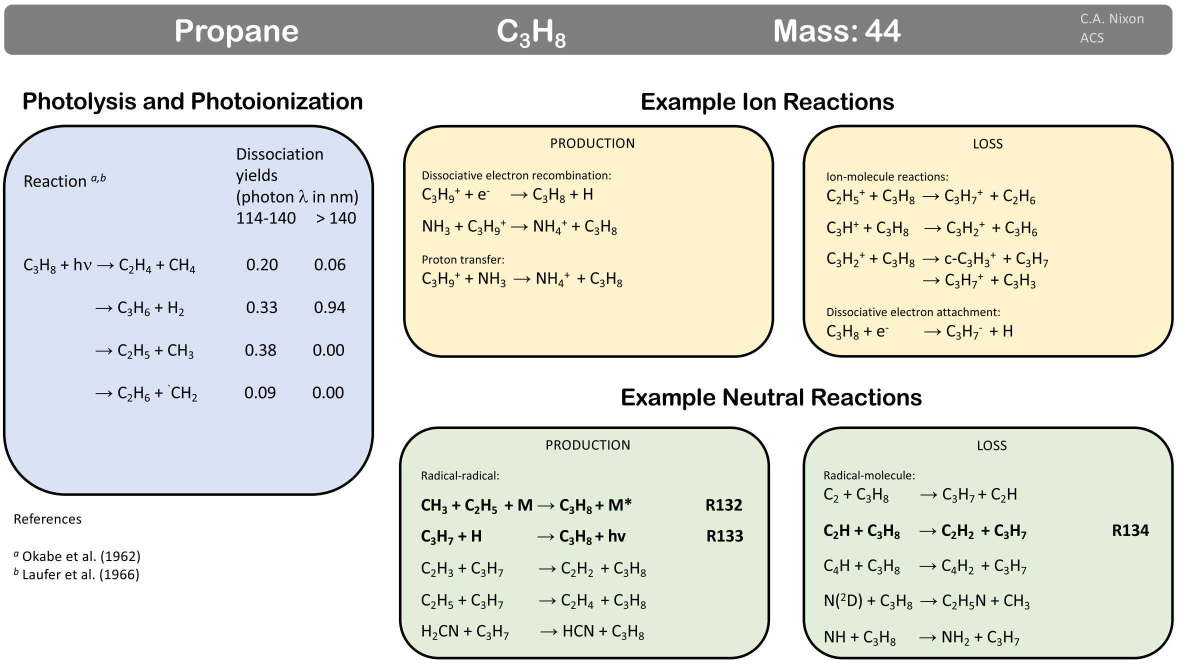

Figure 19. Propane production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

$$CH + C_2H_6 \rightarrow C_3H_6 + H \quad (127)$$

and also lower in the atmosphere by a termolecular reaction:[103]

$$C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M^* \quad (128)$$

Loss. Propene is lost through both photodissociation (Figure 18[321,329,331−334]) and ion reactions, e.g.,[239]

$$C_3H_4^+ + C_3H_6 \rightarrow C_4H_6^+ + C_2H_4 \quad (129)$$

$$C_3H_5^+ + C_3H_6 \rightarrow C_4H_7^+ + C_2H_4 \quad (130)$$

In the lower atmosphere, propene is predicted to be lost through a termolecular reaction with H atom addition:[103]

$$H + C_3H_6 + M \rightarrow C_3H_7 + M^* \quad (131)$$

Future Directions. Propene, as an alkene, may also undergo polymerization to form polypropylene, a notable and widespread plastic used on Earth. Most likely polyynes in Titan's atmosphere are not pure polymers of a single repeated monomer type (ethylene, propylene, etc.) but rather an assorted mixture of many types, with the lighter, more abundant alkenes more heavily represented than larger, heavier units. Further research into polymerization of mixed monomers will yield insights into the formation of Titan's haze.

Propane. Propane (C_3H_8) was detected contemporaneously with propyne (CH_3CCH) by *Voyager*'s IRIS instrument[316] via an infrared band at 748 cm^{-1} and subsequently confirmed by ground-based observations[335] and with *Cassini* CIRS.[163,286,336]

Production. A significant pathway for the production of propane is by addition of CH_3 to C_2H_5 (Figure 19):[337,338]

$$C_2H_5 + CH_3 + M \rightarrow C_3H_8 + M^* \quad (132)$$

It is also formed to a lesser extent by the association reaction[103,339]

$$C_3H_7 + H \rightarrow C_3H_8 + h\nu \quad (133)$$

Loss. Propane is primarily lost in the upper atmosphere by photolysis to propene, but it participates in other reactions as shown in Figure 19. Propane also undergoes H abstraction by ethynyl to recycle acetylene:[340]

$$C_3H_8 + C_2H \rightarrow C_3H_7 + C_2H_2 \quad (134)$$

However, the fate of C_3H_7 is largely to react with H to reform propane.[103]

Future Directions. While the chemistry of propane remains relatively well-known, its role in cloud formation and lake composition on Titan remains to be fully explored. Quantum-mechanical analysis of propane's 23 infrared-active bands[336] remains incomplete, preventing accurate modeling at high resolution for these bands. However, in recent years the pseudolinelist technique has proved useful for providing practical absorption coefficients across a wide bandwidth for calculation at medium resolution.[341]

Diacetylene. The presence of diacetylene (C_4H_2, butadiyne) was inferred from infrared spectroscopy of Titan's atmosphere with *Voyager*'s IRIS instrument[342] via emission bands at 220 and 628 cm^{-1}. At present, it remains the only C_4 hydrocarbon species confirmed in Titan's atmosphere (although it should be noted that the nitrile CH_3C_3N, detected with ALMA,[168] also has four carbon atoms).

Production. Diacetylene can be produced by the aforementioned reaction of the ethynyl radical with acetylene (reaction 63) or by stepwise addition to acetylene:[103,283,343]

$$CH + C_2H_2 \rightarrow C_3H_2 + H \quad (135)$$

$$^3CH_2 + C_3H_2 \rightarrow C_4H_3 + H \quad (136)$$

$$CH_3 + C_4H_3 \rightarrow C_4H_2 + CH_4 \quad (137)$$

Loss. Diacetylene may undergo ionization to $C_4H_2^+$ (Figure 20)[344,345] and subsequent loss to processes such as[239]

$$C_4H_2^+ + C_2H_4 \rightarrow C_6H_5^+ + H \quad (138)$$

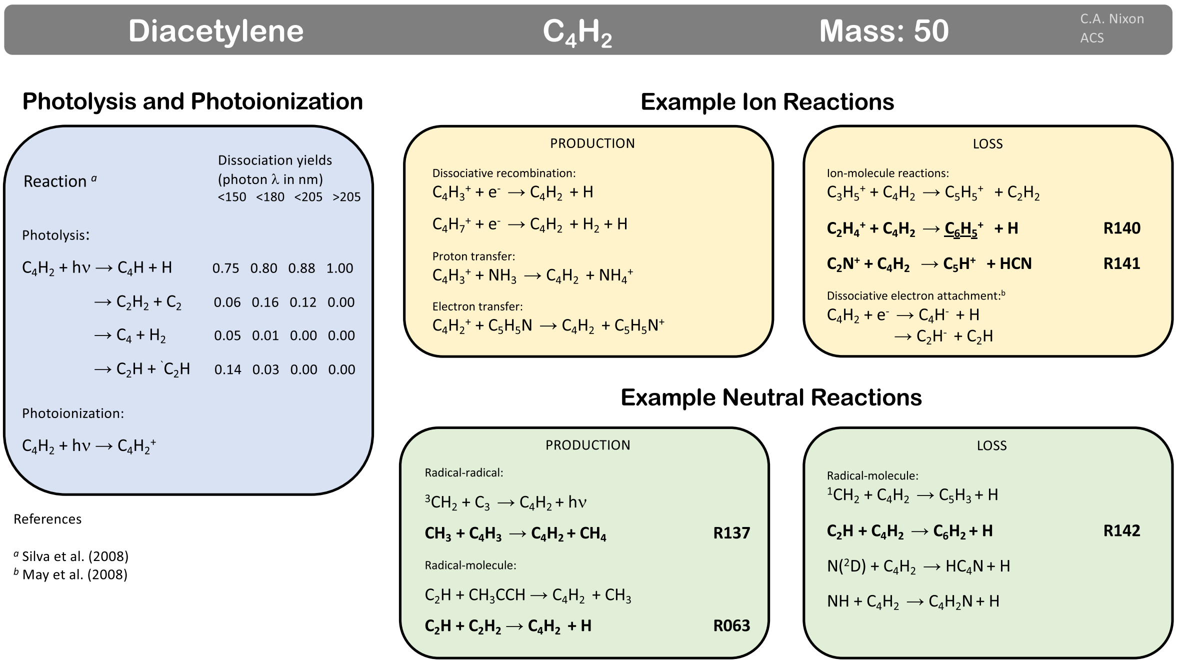

Figure 20. Diacetylene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

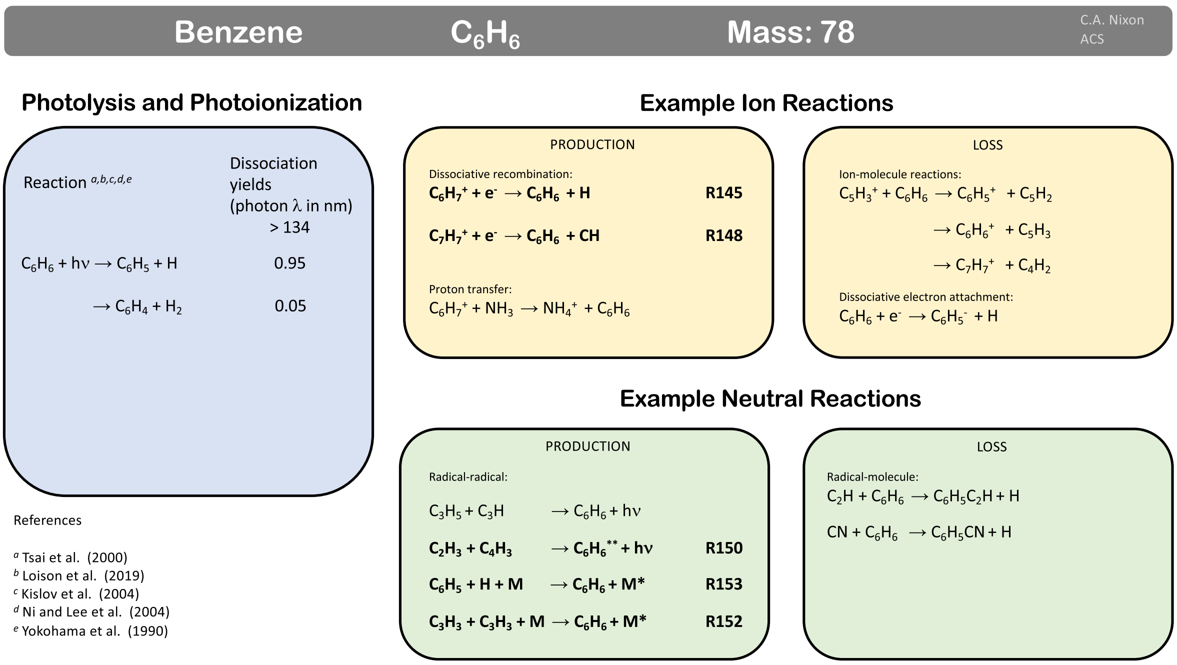

Figure 21. Benzene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

$$C_4H_2^+ + C_2H_4 \rightarrow C_4H_4^+ + C_2H_2 \quad (139)$$

while neutral C_4H_2 may be lost through ion reactions, including[242,346]

$$C_2H_4^+ + C_4H_2 \rightarrow C_5H_3^+ + CH_3 \quad (140)$$

$$C_2N^+ + C_4H_2 \rightarrow C_5H^+ + HCN \quad (141)$$

Insertion of ethynyl is a way to lengthen the polyyne chain from diacetylene to triacetylene:[347]

$$C_2H + C_4H_2 \rightarrow C_6H_2 + H \quad (142)$$

Future Directions. To date, the triacetylene molecule (C_6H_2) has remained elusive on Titan, despite its detection in space at high relative abundances compared to C_4H_2.[348] Detection of triacetylene would help to clarify the importance of the C_6H radical, which contributes to the depletion of methane in photochemical models along with the smaller related radicals C_2H and C_4H, as well as the efficacy of polyyne formation in general.

Benzene. Benzene (c-C_6H_6) (Figure 21)[102,349−352] was the second new species detection on Titan made by the *Infrared Space Observatory* (ISO) in 2003,[49] via its strong hydrogen bending mode at 674 cm^{-1}. Benzene was the first cyclic (closed-ring) molecule to be detected on Titan and remains the only

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confirmed aromatic molecule (molecules with delocalized π bonding electrons). The detection of benzene is highly significant since it provides a measurement of the basic six-membered ring from which larger, multiring molecules can be formed,[353,354] building toward macromolecular haze particles (see discussion later in this review).

Production. In the upper atmosphere (800−950 km), a significant pathway for creation of benzene is dissociative recombination (DR) of the phenylium ion ($C_6H_7^+$). Phenylium is created through the reactions[92,102]

$$C_6H_5^+ + H_2 \rightarrow C_6H_7^+ + h\nu \quad (143)$$

$$C_4H_5^+ + C_2H_4 \rightarrow C_6H_7^+ + H_2 \quad (144)$$

and then forms benzene through the reaction[355]

$$C_6H_7^+ + e^- \rightarrow C_6H_6 + H \quad (145)$$

A second source roughly equal in importance is thought to be formation followed by dissociative recombination of the $C_7H_7^+$ ion (benzylium or tropylium; Figure 22):[102]

$$C_5H_5^+ + C_2H_2 \rightarrow C_7H_7^+ + h\nu \quad (146)$$

$$C_6H_5^+ + CH_4 \rightarrow C_7H_7^+ + H_2 \quad (147)$$

$$C_7H_7^+ + e^- \rightarrow C_6H_6 + CH. \quad (148)$$

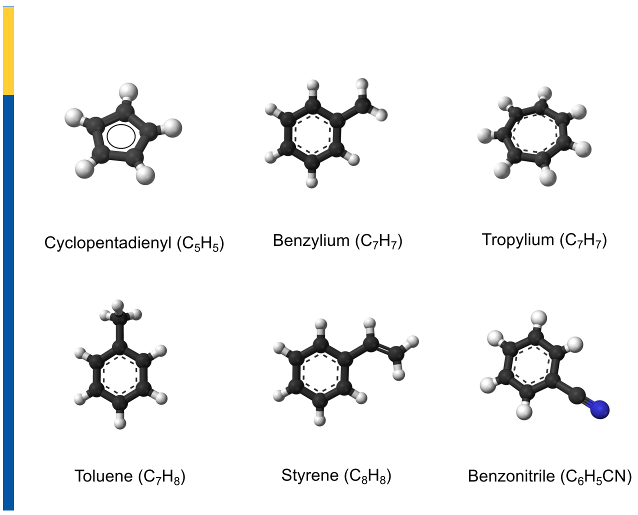

Figure 22. Potential benzene precursor molecules (top) and products (bottom). Molecule images: Wikimedia Commons.

Yet a third ion channel is the DR of $C_8H_{11}^+$ with e^-, leading to benzene plus other hydrocarbon fragments.[102]

Radical chemistry also leads to to benzene, such as C_2 addition to 1,3-butadiene proposed to occur in the ISM:[356]

$$C_2H + C_4H_6 \rightarrow C_6H_6 + H \quad (149)$$

An alternate pathway,

$$C_2H_3 + C_4H_3 \rightarrow C_6H_6^* + h\nu \quad (150)$$

also leads to benzene, but in a highly excited state where it mostly dissociates to $C_6H_5 + H$.[102] Recently, a new pathway via a smaller five-membered-ring radical (cyclopentadienyl, Figure 22) has been proposed by Kaiser et al.:[354]

$$c\text{-}C_5H_5 + CH_3 \rightarrow c\text{-}C_5H_5CH_3 \rightarrow c\text{-}C_6H_7 + H \rightarrow c\text{-}C_6H_6 + 2H \quad (151)$$

However, this has yet to be added to photochemical models to assess its relative importance.

At higher pressures lower in the atmosphere, the three-body reaction combining two propargyl radicals becomes the dominant pathway for creation of benzene:[79,80,92,102]

$$C_3H_3 + C_3H_3 + M \rightarrow C_6H_6 + M^* \quad (152)$$

Loss. Benzene is lost through ionization to the phenylium ion ($C_6H_5^+$) and through photolysis to form phenyl (C_6H_5).[92,357] The phenyl radical then either reforms benzene via[94]

$$C_6H_5 + H + M \rightarrow C_6H_6 + M^* \quad (153)$$

or reacts with other radicals and neutral species, leading to molecules such as toluene ($C_6H_5CH_3$), styrene ($C_6H_5C_2H$), and benzonitrile (C_6H_5CN).[358]

Future Directions. Benzene is a highly significant molecule as the precursor to larger, multiring molecules. Further studies of its creation and loss mechanisms, especially pathways to larger molecules (Figure 22),[353] are important future directions.

Nitrogen Compounds. Nitrogen compounds are formed by chemical combination of dissociation products from initial N_2 and CH_4 and have formulas $C_xH_yN_z$. All of the eight known heteroatomic nitrogen compounds are cyanides, wherein nitrogen is bonded to carbon by a triple bond ($-C{\equiv}N$) and therefore have the formula $C_xH_y(CN)_z$. These are HCN, HNC, CH_3CN, C_2H_3CN, C_2H_5CN, HC_3N, CH_3C_3N, and C_2N_2 (see Figure 23). Other than the light molecules HCN and HNC, the remaining molecules are nitriles (organic cyanides).

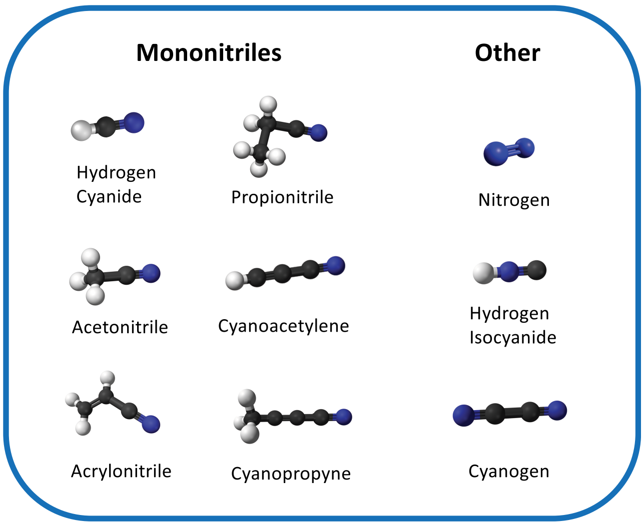

Figure 23. Nitrogen-bearing molecules detected on Titan.

Hydrogen isocyanide (HNC) is less stable than hydrogen cyanide (HCN) and is converted exothermically to HCN as it descends in the atmosphere. This leads to a predicted steep decrease in abundance with increasing pressure[359] and its present nondetection at lower altitudes.

In the lower atmosphere, nitrogen has always been found to date to be triple-bonded in the terminal position of a molecule: other types of species (amines, imines, etc.) have not yet been detected. We will return to the topic of what additional nitrogen compounds may be waiting to be discovered in a later section.

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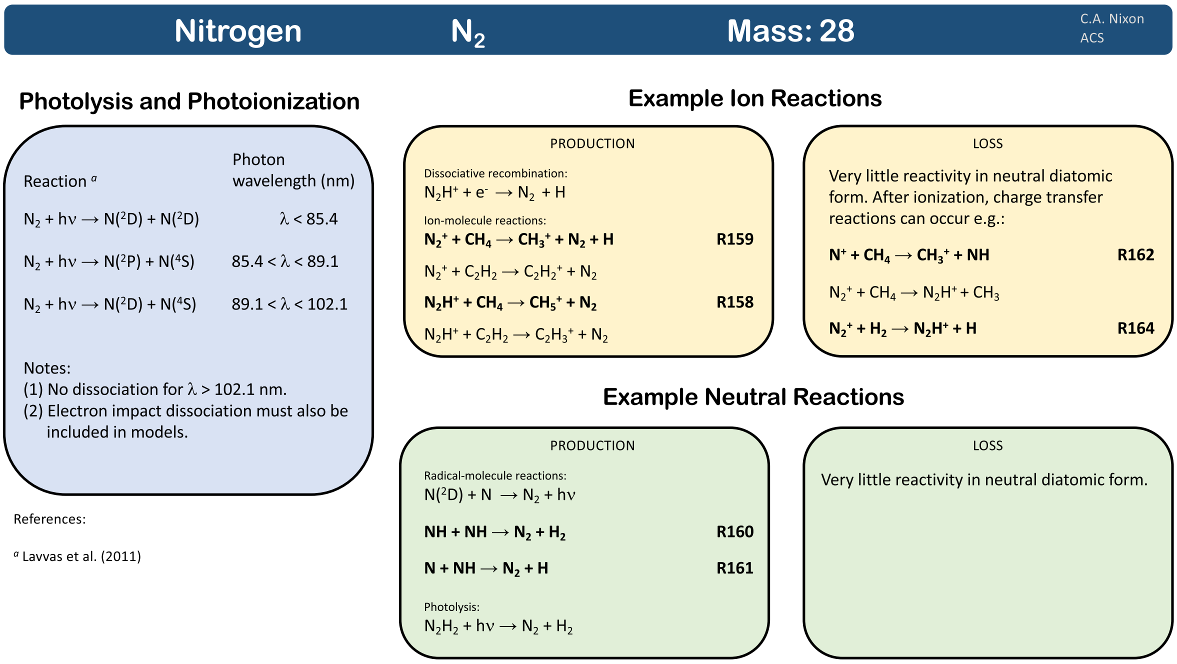

Figure 24. Production and loss pathways for molecular nitrogen. Reactions numbered and shown in bold correspond to discussion in the text.

The chemistry of known N-bearing molecules in the neutral atmosphere is now summarized.

Nitrogen. A major but unobserved constituent in Titan's atmosphere was necessitated by the observed collisional broadening of methane spectral lines:[360] this was hypothesized to be molecular nitrogen,[361] which would be invisible at visible and longer wavelengths. The first conclusive observations of nitrogen were by *Voyager 1*'s UVS instrument, which detected dayside airglow at 96 and 98 nm and longer-wavelength absorptions with occultation measurements.[362,363] Measurements of nitrogen were greatly extended by *Cassini*'s UVIS instrument.[26,364−367]

Production. The origin of nitrogen in Titan's atmosphere has been long debated and is not the subject of this review. In brief, two major theories exist: enclathratization of N_2 gas in the protosolar nebula[368] and accretion in the form of NH_3 ice followed by later photodissociation to eventually form N_2 through a reaction cascade:[369]

$$NH_3 + h\nu \rightarrow NH_2 + H \quad (154)$$

$$2NH_2 + M \rightarrow N_2H_4 + M^* \quad (155)$$

$$N_2H_4 + H \rightarrow N_2H_3 + H_2 \quad (156)$$

$$2N_2H_3 \rightarrow 2NH_3 + N_2 \quad (157)$$

The latter scenario is currently favored due to the low temperatures in the subnebula required to capture molecular nitrogen directly. Variations on the theory include impact conversion of either NH_3 or ammonium sulfate ($(NH_4)_2SO_4$) to N_2.[370,371]

N_2 can also be recycled by recombination or proton transfer of one its ions:[239,242,372]

$$N_2H^+ + CH_4 \rightarrow CH_5^+ + N_2 \quad (158)$$

$$N_2^+ + CH_4 \rightarrow CH_3^+ + N_2 + H \quad (159)$$

or through recycling of one of its radicals:[103,373]

$$NH + NH \rightarrow N_2 + H_2 \quad (160)$$

$$N + NH \rightarrow N_2 + H \quad (161)$$

Loss. Molecular nitrogen is dissociated and/or ionized by short-wavelength solar radiation at $\lambda < 127$ nm,[374] Saturn magnetosphere electrons,[375] and galactic cosmic rays (GCRs)[177−180] (Figure 24).[173]

Nitrogen ions react with abundant neutrals, including CH_4 and H_2:[242,376]

$$N^+ + CH_4 \rightarrow CH_3^+ + NH \text{ (and others)} \quad (162)$$

$$N^+ + H_2 \rightarrow NH^+ + H \quad (163)$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \quad (164)$$

It can recycle to N_2 through reaction with hydrogen, methane, and other hydrocarbons, e.g.,[242]

$$N_2^+ + H_2 \rightarrow H_2^+ + N_2 \quad (165)$$

$$N_2^+ + CH_4 \rightarrow CH_3^+ + N_2 + H \text{ (and others)} \quad (166)$$

$$N_2^+ + C_2H_2 \rightarrow C_2H_2^+ + N_2 \quad (167)$$

$$N_2^+ + C_2H_6 \rightarrow CH_3^+ + N_2 + CH_3 \text{ (and others)} \quad (168)$$

However, molecular nitrogen in the un-ionized state has very low reactivity, which in part contributes to its great abundance and significant longevity in the atmosphere.

Isotopes. Since $^{14}N_2$ and $^{14}N^{15}N$ have significantly different UV cross sections,[377] it is important to correctly account for both isotopes and the wavelength variation of the solar spectrum to arrive at correct dissociation rates. Self-shielding by the more abundant $^{14}N^{14}N$ is thought to reduce photolysis rates relative to the less abundant, less shielded $^{14}N^{15}N$, causing a lower $^{14}N/^{15}N$ ratio in nitrogen atoms than in the original molecules. Since significant amounts of atomic nitrogen go on to form nitriles, this skew toward increased production of ^{15}N may explain the lower $^{14}N/^{15}N$ ratio in nitriles than in N_2 itself.[377−379]

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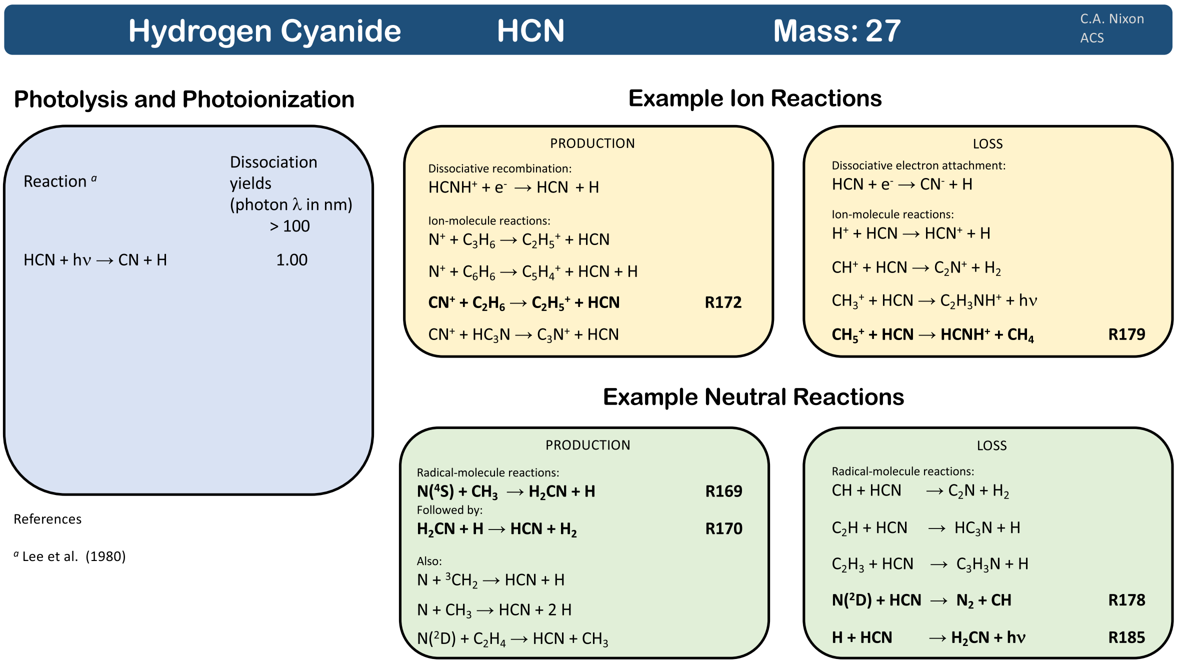

Figure 25. Hydrogen cyanide production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Future Directions. The dissociation and reaction pathways for N_2 and its daughter ions and radicals remain one of the better known areas of Titan chemistry. However, gaps remain, in particular whether nitrogen exists in chemicals such as amines and imines or if it is incorporated into heterocyclic ring molecules. This is further discussed in a later section.

Hydrogen Cyanide. Hydrogen cyanide was first detected by *Voyager* 1 IRIS[380] through its strong infrared emission at 712 cm^{-1} and later at submillimeter wavelengths from ground-based observatories.[164,381−383] Although it is a relatively simple molecule that has been included in photochemical models for more than four decades, gaps in our knowledge of HCN formation may still exist, and new pathways have been identified recently.[384]

Production. HCN is primarily produced in the upper atmosphere by the reaction of methane and nitrogen dissociation products (Figure 25):[385]

$$N(^4S) + CH_3 \rightarrow H_2CN + H \quad (169)$$

$$H_2CN + H \rightarrow HCN + H_2 \quad (170)$$

$$H_2CN + h\nu \rightarrow HCN + H \quad (171)$$

It also may be reformed from its ion by ion−molecule reactions, e.g.,[239]

$$CN^+ + C_2H_6 \rightarrow C_2H_5^+ + HCN \quad (172)$$

In the lower atmosphere, reactions with CN radicals become important:[91,202,203,386]

$$CN + CH_4 \rightarrow HCN + CH_3 \quad (173)$$

$$CN + C_2H_6 \rightarrow HCN + C_2H_5 \quad (174)$$

$$CN + C_3H_8 \rightarrow HCN + C_3H_7 \quad (175)$$

along with photodissociation of C_2H_3CN (Figure 30)[387] and reaction of other nitriles with H:[91,103]

$$H + C_2N_2 \rightarrow HCN + CN \quad (176)$$

$$H + H_2CN \rightarrow HCN + H_2 \quad (177)$$

Loss. At high altitudes ($z \geq 1000$ km) HCN is primarily destroyed by reaction with $N(^2D)$:[91,103]

$$HCN + N(^2D) \rightarrow CH + N_2 \quad (178)$$

HCN may also be lost in a two-step process, beginning with proton transfer from a lower-proton-affinity molecule, e.g.,[103]

$$CH_5^+ + HCN \rightarrow HCNH^+ + CH_4 \quad (179)$$

followed by dissociative recombination:[373]

$$HCNH^+ + e^- \rightarrow CN + 2H \quad (180)$$

Lower in the atmosphere, radical reactions and photolysis become important:[91]

$$HCN + C_2 \rightarrow C_3N + H \quad (181)$$

$$HCN + C_2N \rightarrow C_4N_4 + H \quad (182)$$

As noted by previous authors, the C≡N triple bond is extremely stable, and therefore, the CN unit tends to persist when HCN is photolyzed, being incorporated into heavier nitriles, e.g.:

$$HCN + h\nu \rightarrow H + CN \quad (183)$$

$$C_2H_2 + CN \rightarrow HC_3N + H \quad (184)$$

Also, at low altitudes ($z < 650$ km),[103] H addition can lead to formation of the methylene amidogen radical:

$$HCN + H \rightarrow H_2CN + h\nu \quad (185)$$

Future Directions. Although well-studied for decades, recent work[384,388] has identified new pathways for the formation of HCN in planetary atmospheres for which reaction rates are currently unknown. Theoretical predictions now exist, but experimental confirmation is needed.

HCN has been shown to form cocrystals with hydrocarbons at Titan-relevant temperatures,[389] the study of which will be important for understanding the solids and liquids on the

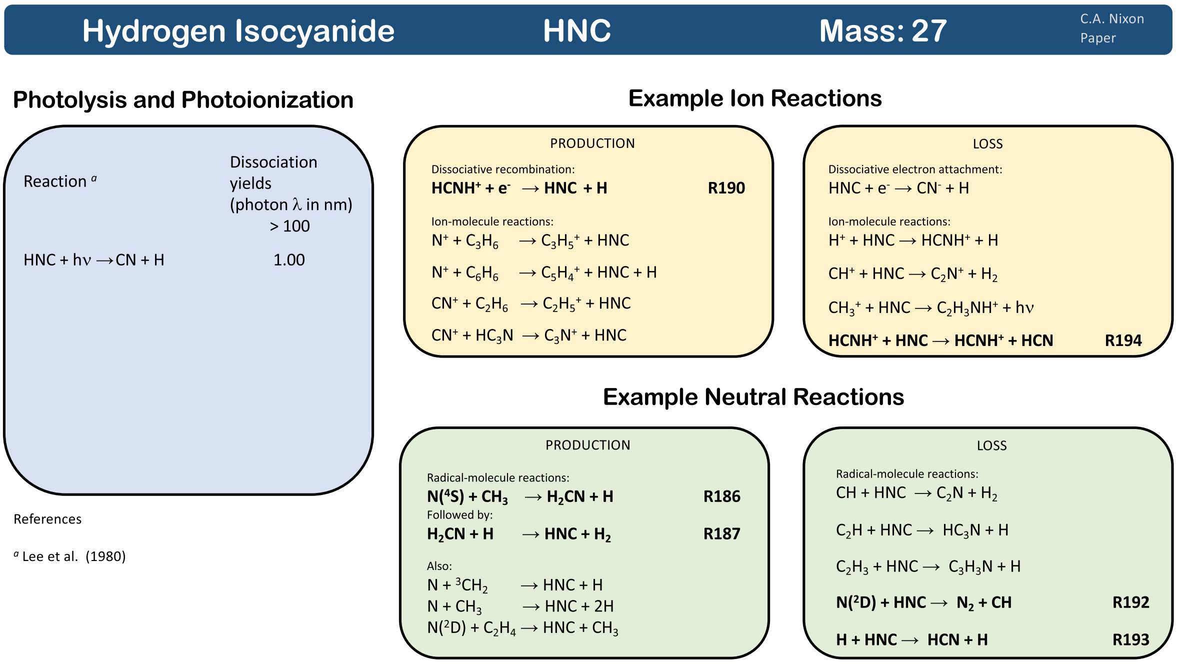

Figure 26. Hydrogen isocyanide production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

surface. HCN, along with HC_3N, has also been implicated in the formation of C_4N_2 in grain-surface chemical reactions,[390] which requires further study to elucidate reaction rates and whether this process is sufficient to explain observed ice spectral properties.[391]

Finally, HCN has been implicated in processes of astrobiological importance. A well-known example is its proposed ability to directly form the nucleobase adenine ($C_5H_5N_5$)[392−395] from the rearrangement (oligomerization) of five HCN molecules. Although the importance of this reaction for the seeding of life on the early Earth has been disputed,[396,397] it may be more prevalent on Titan, where HCN occurs in greater abundance.[398,399] HCN may also have the potential to polymerize into polyimines, structures that may catalyze astrobiologically important reactions.[400] The astrobiological potential of HCN therefore remains under continued investigation.[384,401−403]

Hydrogen Isocyanide. Hydrogen isocyanide, a higher-energy isomer of hydrogen cyanide,[404] was discovered on Titan using the *Herschel* space observatory by its submillimeter transition at 544 GHz[405] and subsequently measured by ALMA as well.[128,359] HNC is readily interconverted to the more stable HCN (releasing 14.4 ± 1.0 kcal/mol)[406] and therefore is predicted to have a steeply diminishing mixing ratio profile with altitude.[98,103]

Production. HNC is produced by the same neutral reactions as HCN:

$$N(^4S) + {}^3CH_2 \rightarrow HNC + H \quad (34\%) \tag{186}$$

$$H + H_2CN \rightarrow HNC + H_2 \quad (64\%) \tag{187}$$

where the relative productions are estimated at 1300 km.[90] At 1000 km, reaction 186 becomes dominant. Note that there are two important production pathways for H_2CN:

$$N(^4S) + CH_3 \rightarrow H_2CN + H \tag{188}$$

$$CH_2NH + h\nu \rightarrow H_2CN + H \tag{189}$$

with reaction 188 dominating in the thermosphere and reaction 189 becoming important in the mesosphere and below.[90] Ion pathways may also be similar (see Figure 26),[385] although branching ratios are in most cases more uncertain than for HCN, e.g., through dissociative recombination of $HCNH^+$:[407]

$$HCNH^+ + e^- \rightarrow HNC + H \tag{190}$$

HNC may also be produced as a photodissociation product of C_2H_3CN[387] in the upper atmosphere, and a further production peak may occur due to cosmic ray chemistry at 100−150 km.[98]

Loss. At high altitudes (∼1300 km) the principal loss channels for HNC are[90]

$$N(^2D) + HNC \rightarrow CN_2 + H \tag{191}$$

$$N(^2D) + HNC \rightarrow CH + N_2 \tag{192}$$

while at lower altitudes collisional isomerization to the lower-energy HCN becomes important and is dominant by 600 km:[90]

$$HNC + H \rightarrow HCN + H \quad (z < 1000\text{ km}) \tag{193}$$

$$HNC + HCNH^+ \rightarrow HCN + HCNH^+ \quad (z > 1000\text{ km}) \tag{194}$$

Future Directions. HNC/HCN is now one of two isomer pairs known in Titan's atmosphere (the other being C_3H_4). Studies of the branching ratios and reaction rates leading to and from isomer pairs/triples, etc., are of importance because the less stable isomer(s) may follow different reaction pathways compared to the more abundant molecule(s). Therefore, for a complete understanding of Titan's atmospheric chemistry, all isomers must be included in models. Studies of the vertical ratio between HCN/HNC and CH_3CCH/CH_2CCH_2 may also provide useful information on the abundance of atomic H, as collisions with H can cause conversion between the isomers.

Acetonitrile. Acetonitrile was first detected on Titan in the early 1990s by millimeter wavelength astronomy,[408] followed 10 years later by the first measurement of its vertical profile[164] using the 30 m telescope at IRAM. CH_3CN was the first Titan

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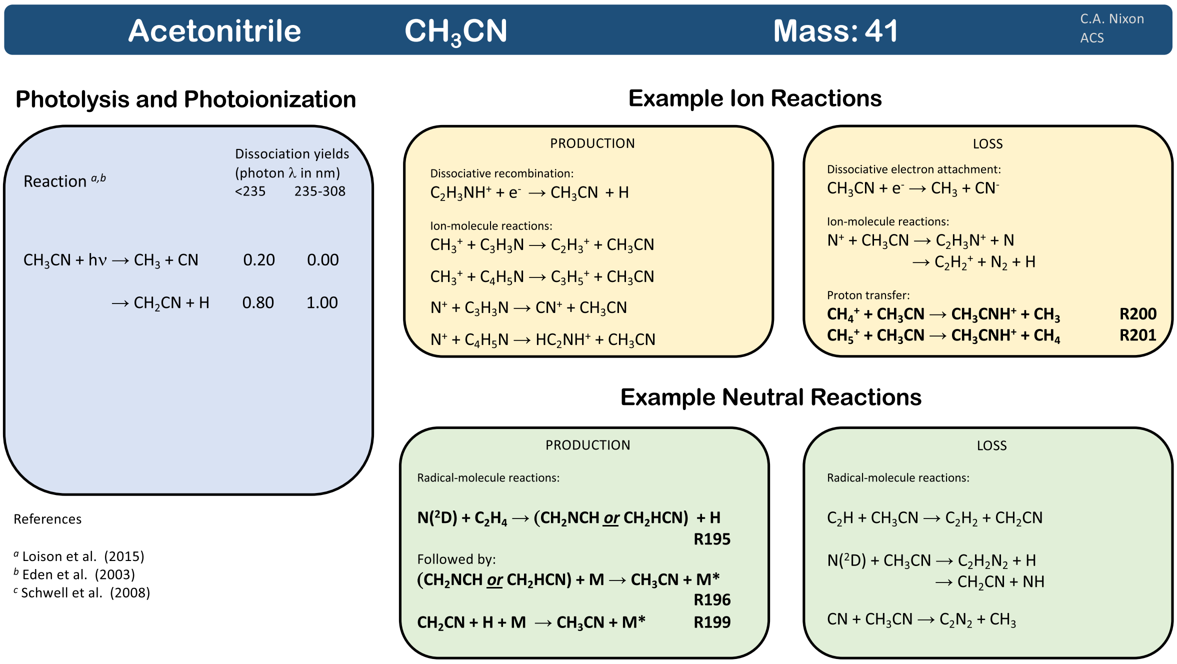

Figure 27. Acetonitrile production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

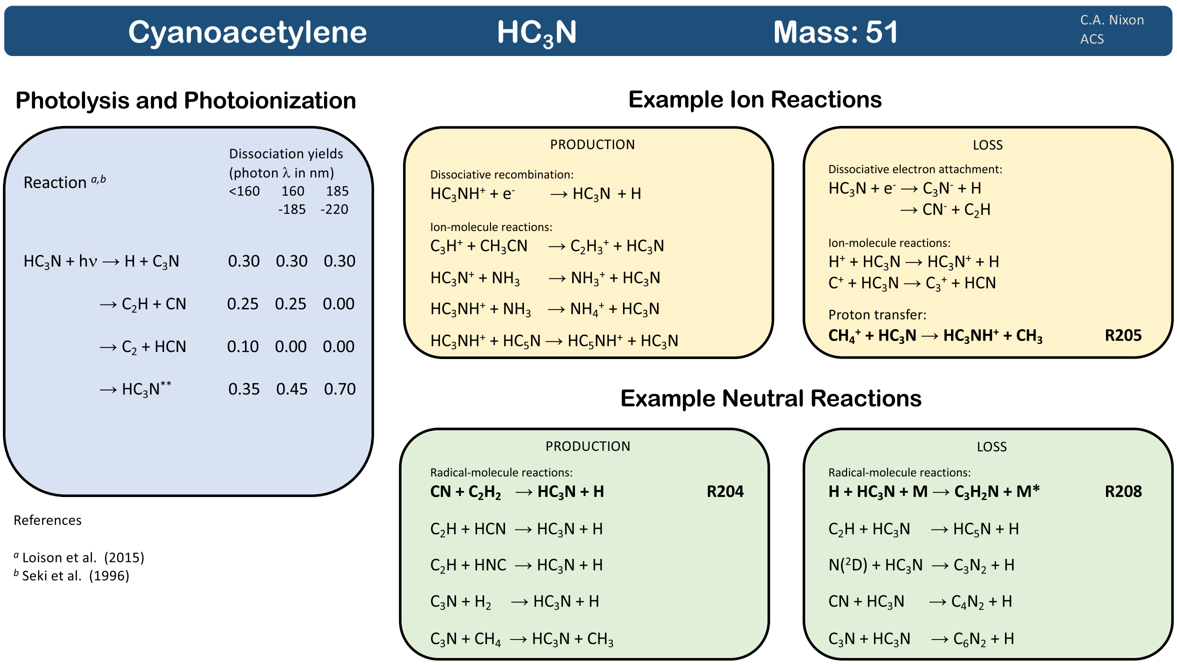

Figure 28. Cyanoacetylene production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

molecule to be first detected at millimeter wavelengths, an astronomical technique that was to yield many other discoveries later with ALMA.

Production. Acetonitrile is produced in the upper atmosphere by the reaction of N radicals with ethylene:[409]

$$N(^2D) + C_2H_4 \rightarrow (c\text{-}CH_2HCN \text{ or } CH_2(N)CH) + H \quad (195)$$

$$(c\text{-}CH_2HCN \text{ or } CH_2(N)CH) + M \rightarrow CH_3CN + M^* \quad (196)$$

and by the termolecular reaction of H with cyanomethyl (CH_2CN) in a chain that begins with acrylonitrile (C_2H_3CN):[98,103]

$$H + C_2H_3CN + M \rightarrow C_2H_4CN + M^* \quad (197)$$

$$H + C_2H_4CN \rightarrow CH_2CN + CH_3 \quad (198)$$

$$H + CH_2CN + M \rightarrow CH_3CN + M^* \quad (199)$$

Loss. The major loss mechanism for acetonitrile is proton transfer from another ion to form CH_3CNH^+, e.g.,[410]

$$CH_4^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_3 \quad (200)$$

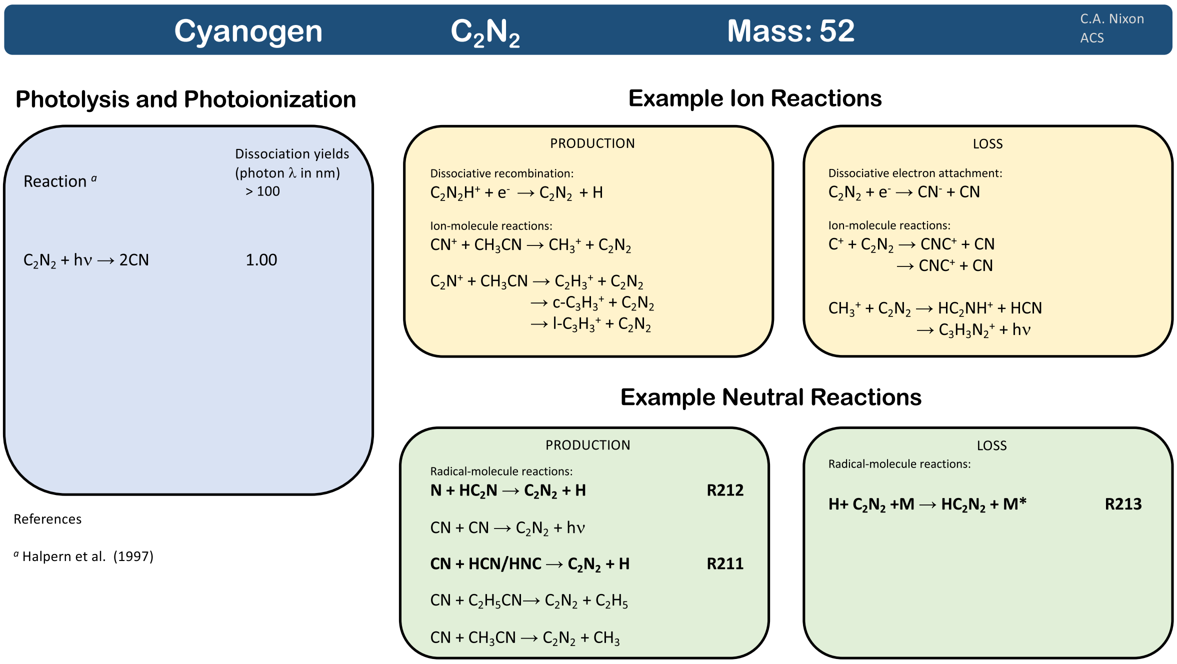

Figure 29. Cyanogen production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

$$CH_5^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_4 \quad (201)$$

followed by dissociative recombination:[411,412]

$$CH_3CNH^+ + e^- \rightarrow HNC + CH_3 \quad (202)$$

$$CH_3CNH^+ + e^- \rightarrow HCN + {}^3CH_2 + H \quad (203)$$

and in the lower atmosphere by photolysis[413,414] (Figure 27).[98,415,416]

Future Directions. Acetonitrile, like many other simple molecules, has been implicated in formation of a cocrystal with acetylene,[417] providing an interesting avenue for further investigation of its solid-phase properties, with possible implications for cloud particle growth.

Cyanoacetylene. Cyanoacetylene (HC_3N, propynenitrile) was first detected in Titan's atmosphere by *Voyager* IRIS in the infrared[342] at 500 and 663 cm^{-1}, following a prediction by Capone et al.[418] Cyanoacetylene, like diacetylene and cyanogen, was found in 1980 to be greatly enhanced over Titan's northern (winter) pole, which was interpreted as evidence of a global stratospheric circulation cell. Gases such as HC_3N with relatively short photochemical lifetimes (compared to a Titan year) have volume mixing profiles with steep vertical gradients at most latitudes, decreasing in a downward direction as the gases become depleted and diluted. However, the presence of a strong downward motion from the mesosphere (∼500 km) causes enrichment in trace species to show up much lower down in the lower stratosphere (∼100 km).

Production. Cyanoacetylene is produced above 1000 km by the reaction of acetylene with CN radical from photolysis of HCN (see Figure 28):[98,202,203,419]

$$C_2H_2 + CN \rightarrow HC_3N + H \quad (204)$$

and to a lesser extent by photodissociation of acrylonitrile (see Figure 30).

Loss. As with other nitriles, the principal loss pathway for cyanoacetylene in the upper atmosphere is proton transfer to form HC_3NH^+, e.g.,[239]

$$CH_4^+ + HC_3N \rightarrow HC_3NH^+ + CH_3 \quad (205)$$

followed by dissociative recombination to break up the molecule:[412]

$$HC_3NH^+ + e^- \rightarrow C_2H_2 + CN \quad (206)$$

On the other hand, photolysis is not a significant loss channel, since C_3N is thought to rapidly recycle back to HC_3N through reaction with methane:[98]

$$C_3N + CH_4 \rightarrow HC_3N + CH_3 \quad (207)$$

While HC_3N does react without a barrier with radicals such as CN and C_2H, the main loss channel in the neutral atmosphere is thought to be successive hydrogen addition:[98]

$$HC_3N + H + M \rightarrow H_2C_3N + M^* \quad (208)$$

$$H_2C_3N + H \rightarrow HCN + C_2H_2 \quad (209)$$

$$H_2C_3N + H + M \rightarrow C_2H_3CN + M^* \quad (210)$$

Future Directions. In interstellar space (e.g., molecular clouds such as TMC-1), cyanopolyynes of the form HC_xN have been detected with $x = 1, 3, 5, 7, 9, 11$.[420−422] HC_5N has been sought but not yet detected in Titan's neutral atmosphere. Detection of this molecule may provide some clues as to the relative abundances of cyanopolyynes versus N-heterocycles.

Cyanogen. Cyanogen (C_2N_2), like cyanoacetylene, was first detected in Titan's atmosphere by *Voyager* IRIS in the infrared[342] at 233 cm^{-1}.

Production. Cyanogen is thought to be produced mainly by addition of CN to HNC,

$$CN + HNC \rightarrow C_2N_2 + H \quad (211)$$

and through the radical−radical reaction[98]

$$N + HCCN \rightarrow C_2N_2 + H \quad (212)$$

via the intermediate adduct NCHCN. Neither of these reactions is expected to have an entrance barrier,[98,423,424] while the

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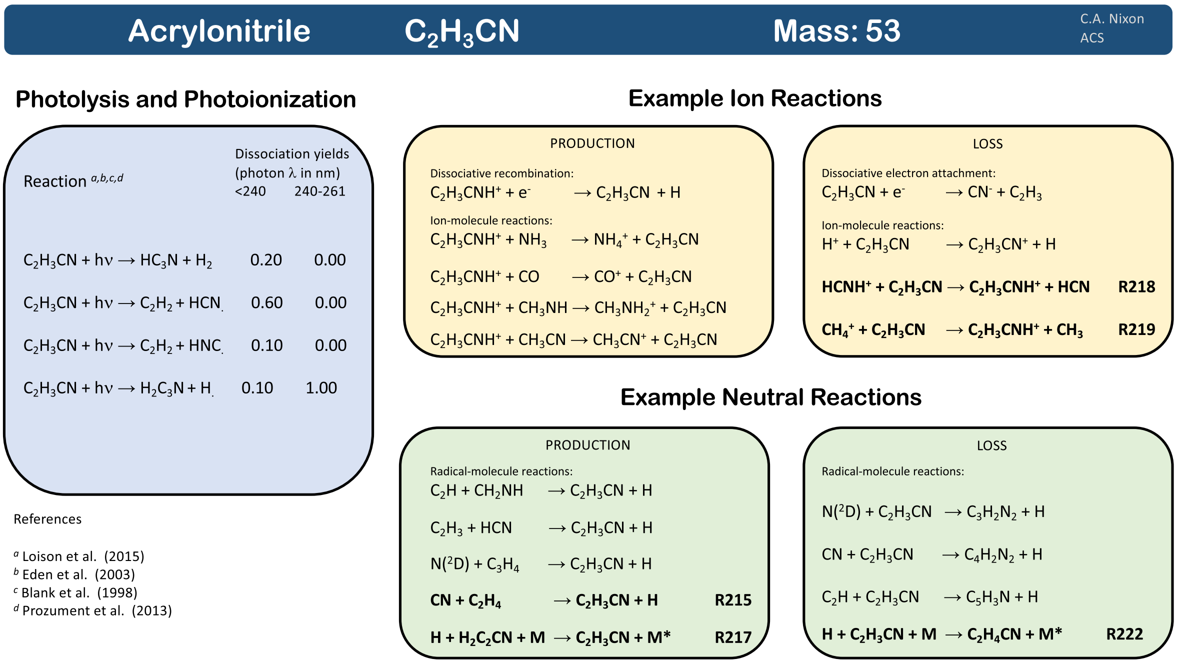

Figure 30. Acrylonitrile production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

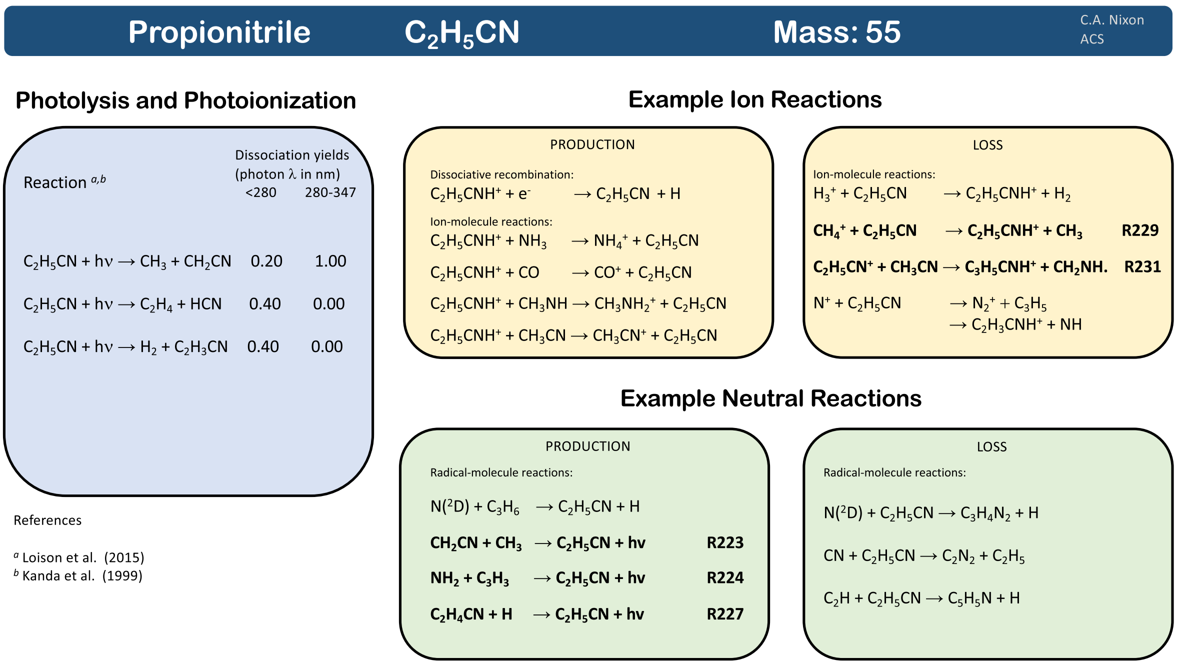

Figure 31. Propionitrile production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

reaction of CN with HCN is inefficient due to the low rate constant.[425−427]

Loss. Cyanogen is lost by photodissociation (Figure 29)[428] and by H addition (with an entrance barrier of ∼14−30 kJ/mol):[98]

$$H + C_2N_2 + M \rightarrow HC_2N_2 + M^* \quad (213)$$

$$H + HC_2N_2 \rightarrow 2HCN \quad (214)$$

Future Directions. A larger cousin to cyanogen, dicyanoacetylene (C_4N_2), is likely to exist in Titan's atmosphere, and detection of its ice has been proposed to explain a feature seen in *Voyager* IRIS and *Cassini* CIRS spectra at 478 cm^{-1},[391,429,430] although a lack of detection of the corresponding gas emission at 471 cm^{-1} has remained puzzling. Anderson et al.[390] proposed a possible explanation by way of ice grain surface chemistry combining HCN and HC_3N, but further laboratory and perhaps in situ experimental measurements are required to verify this hypothesis. For the time being, C_2N_2 remains the only dicyanide molecule known in Titan's atmosphere.

Acrylonitrile. Acrylonitrile (C_2H_3CN) was the second molecule to be discovered on Titan at millimeter wavelengths using ALMA,[166] following the detection of propionitrile,[167] which is discussed in the next section.

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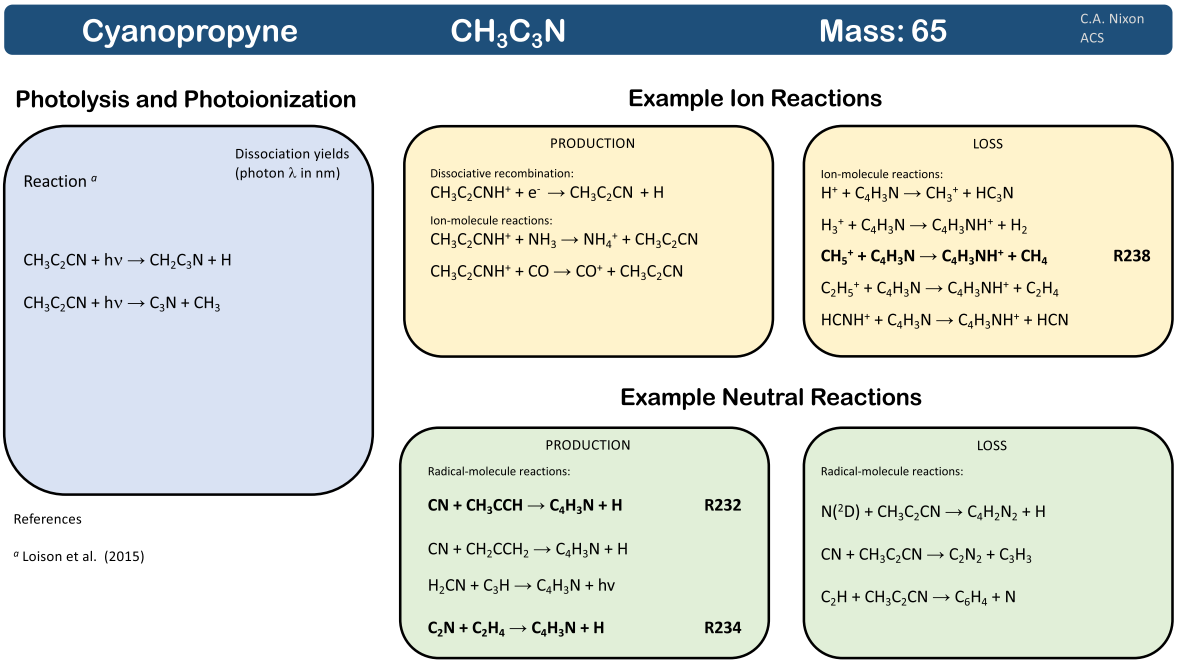

Figure 32. Cyanopropyne production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

Production. Acrylonitrile (see Figure 30)[98,415,431,432] is produced above 800 km by substitution of the CN radical onto ethylene:[202,203]

$$C_2H_4 + CN \rightarrow C_2H_3CN + H \tag{215}$$

Below 800 km, acrylonitrile may be produced by the following termolecular reaction chain:[98,103]

$$H + HC_3N + M \rightarrow H_2C_2CN + M^* \tag{216}$$

$$H + H_2C_2CN + M \rightarrow C_2H_3CN + M^* \tag{217}$$

Loss. In a similar manner to HCN, HC_3N, and other nitriles, C_2H_3CN is lost in the ionosphere by the two-step process of proton transfer, e.g.,[433,434]

$$HCNH^+ + C_2H_3CN \rightarrow C_2H_3CNH^+ + HCN \tag{218}$$

$$CH_4^+ + C_2H_3CN \rightarrow C_2H_3CNH^+ + CH_3 \tag{219}$$

followed by dissociative electron recombination:[435]

$$C_2H_3CNH^+ + e^- \rightarrow C_2H_3 + HNC \tag{220}$$

$$C_2H_3CNH^+ + e^- \rightarrow C_2H_2 + HCN + H \tag{221}$$

In the lower atmosphere it may be lost to photodissociation (which tends to recycle acrylonitrile) or by H addition:[94]

$$C_2H_3CN + H + M \rightarrow C_2H_4CN + M^* \tag{222}$$

Future Directions. Several small nitrile molecules, which tend to exhibit polar properties, have been investigated in a theoretical study for the potential to self-organize into spherical vesicles or membranes in nonpolar liquids (e.g., Titan lakes and seas of methane–ethane–nitrogen). These calculations showed that acrylonitrile was the best candidate for forming so-called "azotosomes",[436] which, if experimentally confirmed, could be significant for astrobiology as vesicles (containers) for self-replicating organisms. However, at this time experimental verification of azotosomes is still lacking, while a later study has questioned the ability of these structures to form.[437]

Propionitrile. Propionitrile (C_2H_5CN) was the second molecule to be originally detected using submillimeter astronomy and the first molecule to be detected with ALMA.[167]

Production. Propionitrile has been posited to be produced above 900 km[103] by the following association reactions (see Figure 31):[98,438]

$$CH_3 + CH_2CN \rightarrow C_2H_5CN + h\nu \tag{223}$$

$$C_3H_3 + NH_2 \rightarrow C_2H_5CN + h\nu \tag{224}$$

Another proposed route to propionoitrile formation is[82,439]

$$C_3H_6 + N^* \rightarrow C_2H_5CN + H \tag{225}$$

In the middle atmosphere (400–900 km),[103] successive rounds of hydrogen addition to acrylonitrile via termolecular reactions can produce propionitrile:

$$H + C_2H_3CN + M \rightarrow C_2H_4CN + M^* \tag{226}$$

$$H + C_2H_4CN + M \rightarrow C_2H_5CN + M^* \tag{227}$$

The following termolecular reaction can also occur:[98]

$$CH_3 + CH_2CN + M \rightarrow C_2H_5CNH + M^* \tag{228}$$

Loss. As with other nitriles, the first step in loss of this nitrile in the ionosphere is proton transfer, forming $C_2H_5CNH^+$:

$$CH_4^+ + C_2H_5CN \rightarrow C_2H_5CNH^+ + CH_3 \tag{229}$$

This is followed by either dissociative electron recombination,[440]

$$C_2H_5CNH^+ + e^- \rightarrow CH_2CN + CH_3 + H \tag{230}$$

or ion–neutral reactions such as[323]

$$C_2H_5CNH^+ + CH_3CN \rightarrow C_3H_5CNH^+ + CH_2NH \tag{231}$$

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Future Directions. Propionitrile has been asserted to condense in pure crystalline form in Titan's atmosphere[441] on the basis of an unexplained feature in Titan's far-infrared spectrum. This has been questioned based on vapor pressure of the gaseous form,[442,443] although it is possible that a cocondensed ice containing C_2H_5CN along with other gases may replicate the unexplained "haystack" emission.[444] Further work on spectroscopy will be required to determine if this is a unique solution or if other possibilities exist.

Cyanopropyne. Cyanopropyne (CH_3C_3N) was the fourth molecule to be discovered by ALMA spectroscopy of Titan at millimeter wavelengths,[168] following previous detection in the ISM.[445]

Production. Production pathways for cyanopropyne (see Figure 32) are more uncertain than for many other molecules due to the size and complexity of the molecule, allowing for more numerous reaction pathways, and multiple isomers of C_4H_3N. Pathways involving radicals include the following: (i) CN substitution onto propyne or butadiene:[446,447]

$$CN + CH_3CCH \rightarrow CH_3C_3N + H \quad (232)$$

$$CN + CH_3CCCH_3 \rightarrow CH_3C_3N + CH_3 \quad (233)$$

(ii) C_2N attack on ethylene:[448]

$$C_2N + C_2H_4 \rightarrow CH_3C_3N + H \quad (234)$$

(iii) C_2N attack on acetylene via a three-step process with three-body reactions:[98,448,449]

$$C_2N + C_2H_2 \rightarrow HC_4N + H \quad (235)$$

$$HC_4N + H + M \rightarrow CH_2C_3N + M^* \quad (236)$$

$$CH_2C_3N + H + M \rightarrow CH_3C_3N + M^* \quad (237)$$

Loss. Cyanopropyne is thought to be lost through either photolysis or protonation, e.g.,[103]

$$CH_5^+ + CH_3C_2CN \rightarrow CH_3C_2CNH^+ + CH_4 \quad (238)$$

followed by dissociative electron recombination:[103]

$$CH_3C_2CNH^+ + e^- \rightarrow C_3H_3 + HNC \quad (239)$$

$$CH_3C_2CNH^+ + e^- \rightarrow HC_3N + CH_3 \quad (240)$$

Future Directions. C_4H_3N has at least three stable isomers that have been detected in space.[450,451] Besides the currently detected isomer, cyanopropyne (CH_3C_3N, also called butynenitrile or methylcyanoacetylene), there are also cyanoallene (CH_2C_2HCN)[452] and propargyl cyanide (HC_3H_2CN),[453] both being first detected in the Taurus Molecular Cloud (TMC-1) at radio wavelengths. These provide good targets for detection on Titan, and their measurement would help to constrain photochemical pathways and models. Further more exotic arrangements of the same atoms may also exist and remain to be detected.

Oxygen Compounds. The oxygen chemistry of Titan's atmosphere is apparently straightforward, with few species involved (only CO, CO_2, and H_2O are presently observed; see Figure 33), but it has proven remarkably difficult to replicate in models. Early work showed difficulty in producing sufficient CO from an external flux of water (OH),[44,46] which was originally presumed to come from meteoritic and cometary materials. The discovery of the Enceladus plumes,[454−456] the connection to Saturn's E-ring (or Enceladus torus), and the subsequent finding of both OH and O^+ entering Titan's upper atmosphere[57] apparently from Enceladus, provided an abundant and unambiguous source of oxygen. Subsequent work by Hörst et al.[81] showed that the combination flux of O^+ could finally explain the abundance of CO. In the most recent work, Vuitton et al.[103] showed that OH alone is sufficient to produce the CO via previously unrecognized reaction intermediates.

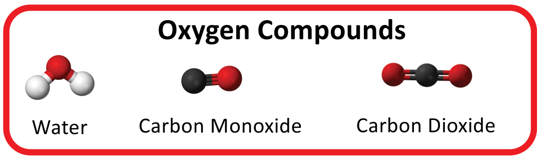

Figure 33. Oxygen-bearing molecules detected on Titan.

Water. Water was first detected in Titan's atmosphere through infrared spectroscopy with ISO[457] through detection of emission lines at 39.4 and 43.9 μm, which was subsequently confirmed with *Cassini* CIRS.[458,459]

Production. Water (Figure 34)[460−462] is thought to mainly be derived by the recombination of OH infalling at the top of the atmosphere, primarily sourced from dissociated Enceladus water, with methane and its dissociation products:

$$OH + CH_3 \rightarrow H_2O + {}^1CH_2 \quad (241)$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \quad (242)$$

Loss. Water is lost to photolysis throughout the atmosphere, reforming hydroxyl (OH). A large fraction of this OH reacts with CH_3 to reform water (see reaction 241). However, OH participates in several other reactions. Above 1000 km, it reacts with $N(^4S)$ to form NO:[97,373]

$$OH + N(^4S) \rightarrow NO + H \quad (243)$$

In the middle atmosphere it reacts with CO to form CO_2:[97]

$$OH + CO \rightarrow CO_2 + H \quad (244)$$

Water also reacts directly with excited-state nitrogen atoms above 900 km:[97,463]

$$H_2O + N(^2D) \rightarrow NH + OH \quad (245)$$

$$H_2O + N(^2D) \rightarrow HNO + H \quad (246)$$

$$H_2O + N(^2D) \rightarrow NO + H_2 \quad (247)$$

Any remaining unreacted water is ultimately lost by condensation in the lower stratosphere.

Future Directions. Due to its low vapor pressure, water remains difficult to measure in Titan's atmosphere. Currently there are large uncertainties in its vertical profile,[458,459] and its latitudinal distribution remains unknown. Further work to better constrain these distributions may help to elucidate the relative importance of meteoritic versus Enceladus sources.[97]

Carbon Monoxide. Carbon monoxide (Figure 35)[464] was first detected on Titan by near-IR spectroscopy, showing an absorbance of CO at 1.6 μm,[465] and the detection was soon confirmed at radio wavelengths.[381] Estimates of its abundance fluctuated throughout the years following its discovery,[466] and the fact that these measurements were often sensitive to different altitudes led to the suggestion that the vertical profile was nonuniform.[381,467] Subsequent measurements with high-sensitivity telescope arrays at Owens Valley and Mauna Kea,

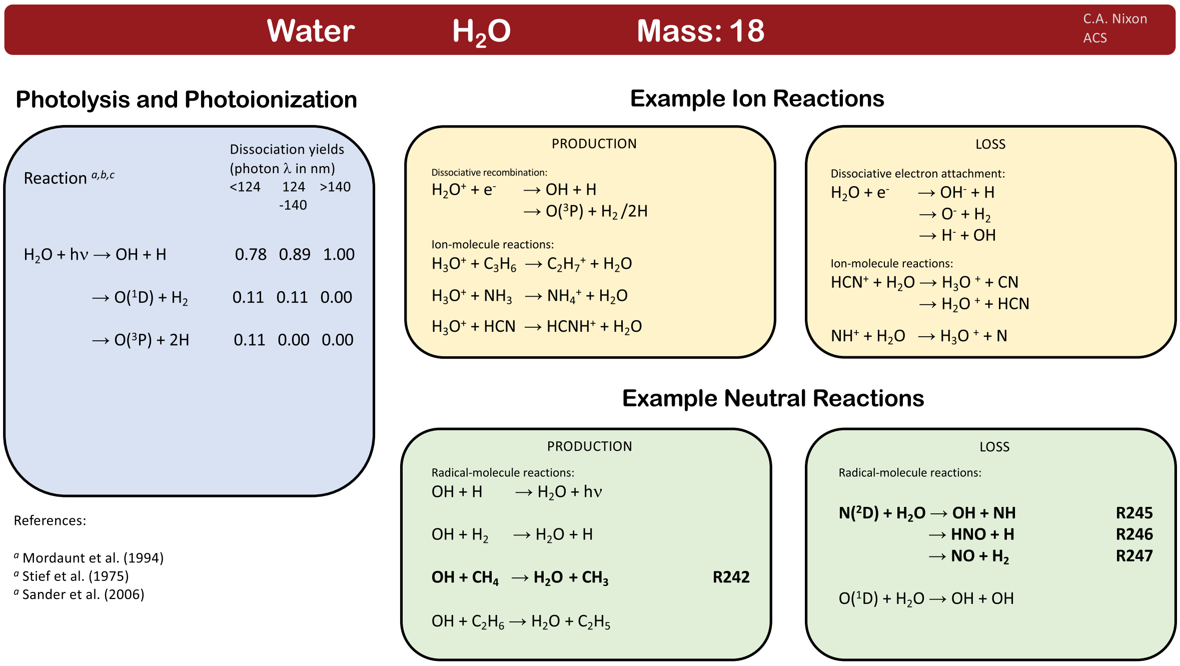

Figure 34. Water production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

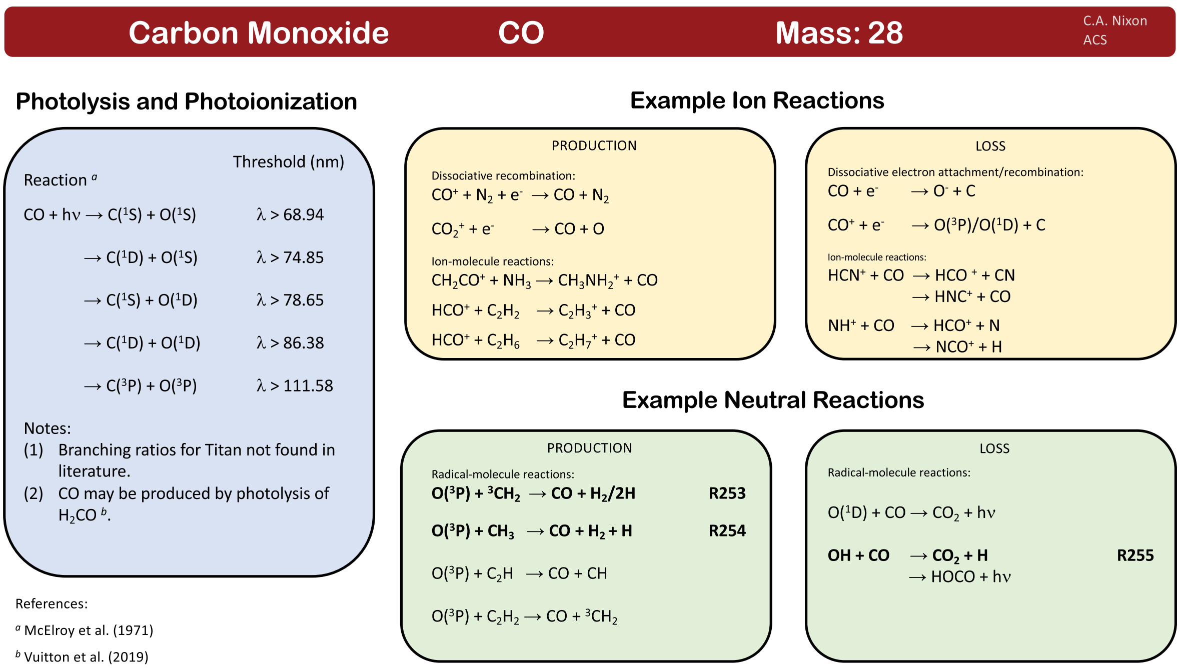

Figure 35. Carbon monoxide production and loss pathways. Reactions numbered and shown in bold correspond to discussion in the text.

however, showed evidence for a uniform profile, converging on a mixing ratio of ∼50 ppb.[468,469]

Recently, high-sensitivity observations with ALMA have narrowed the experimental error to a range of 50 ± 2 ppm,[133] making it the fourth most abundant species in Titan's atmosphere after N_2, CH_4, and H_2. As a triple-bonded molecule, CO once produced is resistant to both photolysis and chemical reaction as well having no loss through condensation, and hence, all evidence available at present points to a uniform vertical profile.

Production. In the model of Vuitton et al.[103] CO is mostly produced via formation of formaldehyde and subsequent photolysis:[470−472]

$$OH + CH_3 \rightarrow CHOH + H_2 \quad (248)$$

$$CHOH + H \rightarrow H_2CO + H \quad (249)$$

$$H_2CO + h\nu \rightarrow CO + H_2 \quad (250)$$

(Formaldehyde may also be created by the reaction of OH with $^3CH_2$, C_2H_4, etc.).

Alternatively, H_2CO may undergo a two-step process to form CO:[223,473]

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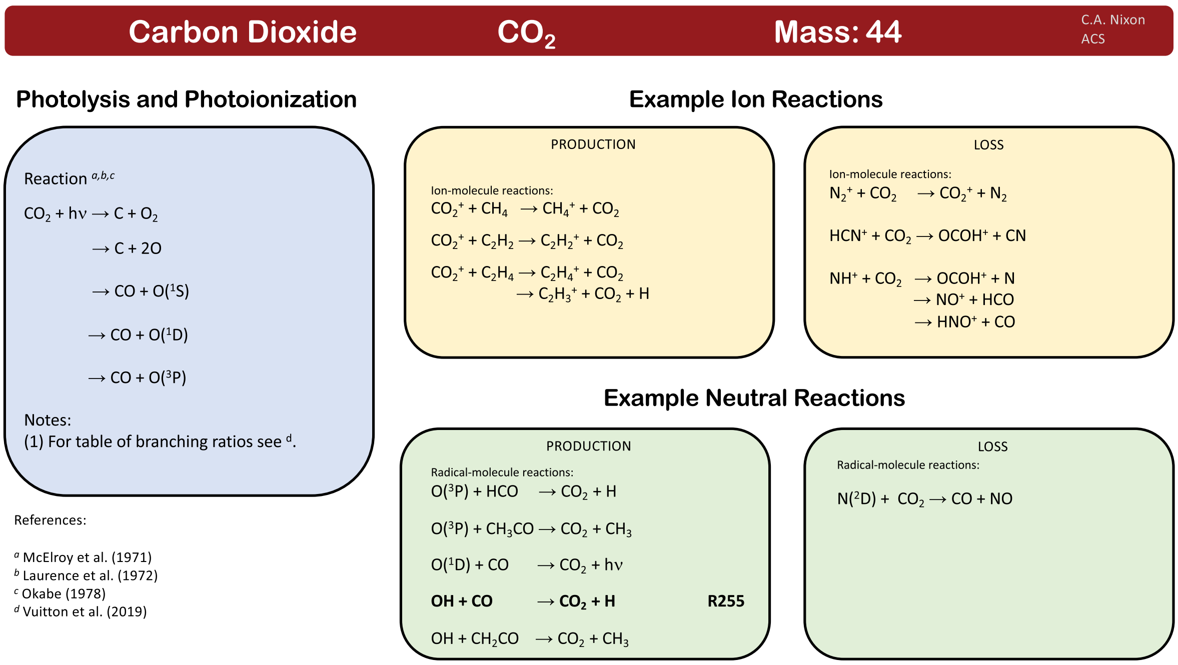

Figure 36. Carbon dioxide production and loss pathways.

$$H_2CO + h\nu \to HCO + H \quad (251)$$

$$HCO + (H/CH_3) \to CO + (H_2/CH_4) \quad (252)$$

(also OH + $^3CH_2$, OH + C_2H_4, etc.). Note that formaldehyde has yet to be detected in Titan's atmosphere.

Lesser routes to CO production may be through reaction of atomic oxygen (deposited to the top of the atmosphere from Enceladus) with methane fragments, e.g.,[81]

$$O(^3P) + {}^3CH_2 \to CO + 2H/H_2 \quad (253)$$

$$O(^3P) + CH_3 \to CO + H_2 + H \quad (254)$$

Loss. CO is primarily lost slowly through reaction with OH to form CO_2:[474]

$$CO + OH \to CO_2 + H \quad (255)$$

CO_2 is in turn lost through condensation.

Future Directions. Laboratory chemistry simulations of Titan's atmosphere have shown that CO may react with methane and nitrogen when sufficiently stimulated, forming amino acids and even nucleobases.[475] This provides an exciting possibility of astrobiology that now requires remote and in situ measurements to confirm.

Carbon Dioxide. Carbon dioxide was one of seven new gas species detected *Voyager* IRIS[476,477] and subsequently by *Cassini* CIRS.[278,478] Unlike shorter-lived chemical chemical species (e.g., HC_3N, C_4H_2), CO_2 exhibits little variation with latitude in the lower stratosphere, lacking a polar enhancement.

Production. CO_2 is thought to be mostly produced from CO + OH, as shown in the previous section (reaction 255). See also Figure 36.[103,464,479]

Loss. The principal loss pathway of CO_2 is through photolysis:[97,480−484]

$$CO_2 + h\nu \to CO + O(^1D) \quad z > 200 \text{ km} \quad (256)$$

$$CO_2 + h\nu \to CO + O(^3P) \quad z < 200 \text{ km} \quad (257)$$

CO_2 is also lost through condensation in the lower stratosphere.

Future Directions. CO_2 remains the most significant atmospheric oxygen repository after CO, but it is shorter-lived and more reactive. It exhibits surprisingly little spatial and seasonal variation in Titan's atmosphere,[127,485] which requires further astronomical monitoring to confirm.

Growth of Large Particles. As hydrocarbon molecules grow to ever-larger sizes, they may take several forms: long chains, fused rings (polycyclic aromatic hydrocarbons (PAHs)), or rings connected by bonds (polyphenyls) (see Figure 37). Nitrogen incorporation is also likely, for example, in the form of polycyclic aromatic nitrogen heterocycles (PANHs). It is thought that eventually larger molecules clump together due to electrostatic forces to form fractal aggregates,[212,486−488] i.e., the Titan haze particles which form the well-known golden haze

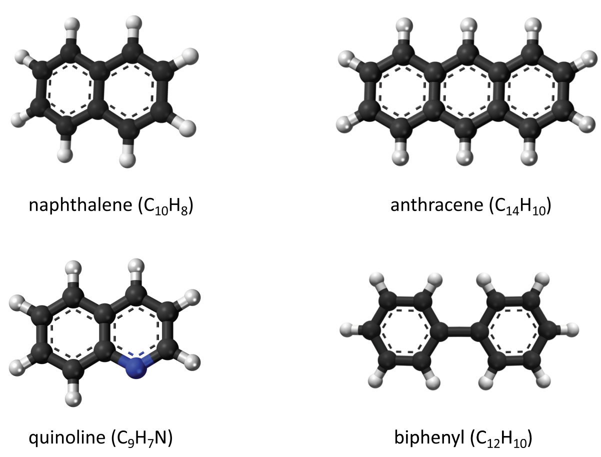

Figure 37. Cyclic or "ring" molecules. Naphthalene: two fused carbon rings. Quinoline: two fused carbon rings with one nitrogen substitution (blue). Anthracene: three fused carbon rings. Biphenyl: two bonded but not fused carbon rings. Image credit: individual PAH graphics from Wikimedia Commons.

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at visible wavelengths. These in turn become the nuclei for stratospheric hydrocarbon ice particles or tropospheric methane raindrops[114−117] and fall to the surface, where they form Titan's dune fields.[118]

The presence of PAHs on Titan has been studied as far back as the 1990s[489] in laboratory experiments. However, despite these predictions, detection of specific PAHs has remained elusive. The closest we have come so far to identification of a unique PAH in Titan's atmosphere was the sighting of a peak at m/z 178 in the CAPS spectrum by Waite et al.,[61] along with another peak at twice the mass(m/z 356). These were tentatively identified as due to anthracene and its dimer (Figure 38), although nonaromatic structures could not be ruled out. Note that the dimer itself may have formed by wall reactions in the instrument, but this would not rule out the fact that anthracene had entered the instrument. Likewise, no polyphenyls or N-heterocycles have been uniquely identified.

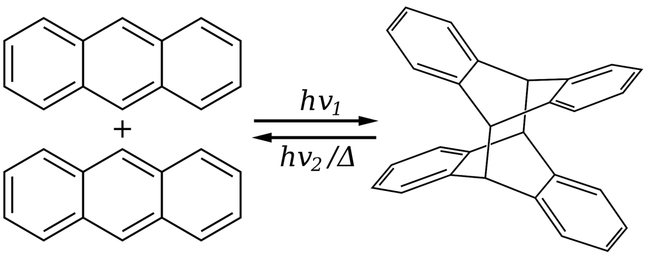

Figure 38. Anthracene dimer (Wikimedia).

Production. The formation of PAHs by addition to benzene rings has been a topic of debate for considerable time. Recently, Kaiser and Hansen[353] categorized possible pathways into five principal mechanisms:

- hydrogen abstraction−C_2H_2 addition (HACA)[490]
- hydrogen abstraction−vinylacetylene addition (HAVA)
- phenyl addition−dehydrocyclization (PAC)
- radical−radical reactions (RRR)
- methylidene addition−cyclization aromatization (MACA)

Each of these offers potential pathways to larger molecules. In brief, the HAVA mechanism, in which vinylacetylene (C_4H_4) adds to aromatic rings (such as benzene) in a barrierless reaction, is thought to be the principal mechanism by which additional six-membered rings are added to existing rings at low temperatures, such as in planetary atmospheres. The other mechanisms offer alternate routes to addition of five- and six-sided rings, predominantly at high temperatures of thousands of kelvins (HAVA, PAC, RRR), although MACA may operate at low temperatures to form indene. The reader is directed to the perspective by Kaiser and Hansen[353] for a full description, which is beyond the scope of this review.

No discussion of aerosol particle growth would be complete without mention of negative ions. The discovery of large negatively charged ions at high altitudes by *Cassini*'s CAPS instrument was one of the major surprises about Titan's atmosphere early in the mission.[60,61,68,69,491,492] Small negative ions may be formed by several processes, including dissociative electron attachment, e.g.,

$$CH_4 + e^- \rightarrow CH_2^- + H_2 \quad (258)$$

$$CH_4 + e^- \rightarrow H^- + CH_3 \quad (259)$$

and radiative attachment to a radical species already formed through photochemistry:[103]

$$CH_3 + e^- \rightarrow CH_3^- + h\nu \quad (260)$$

$$C_4H + e^- \rightarrow C_4H^- + h\nu \quad (261)$$

$$C_6H + e^- \rightarrow C_6H^- + h\nu \quad (262)$$

$$HC_5N + e^- \rightarrow HC_5N^- + h\nu \quad (263)$$

Once H^- is produced, it leads to the creation of some larger negative ions through proton abstraction:[103]

$$C_2H_2 + H^- \rightarrow C_2H^- + H_2 \quad (264)$$

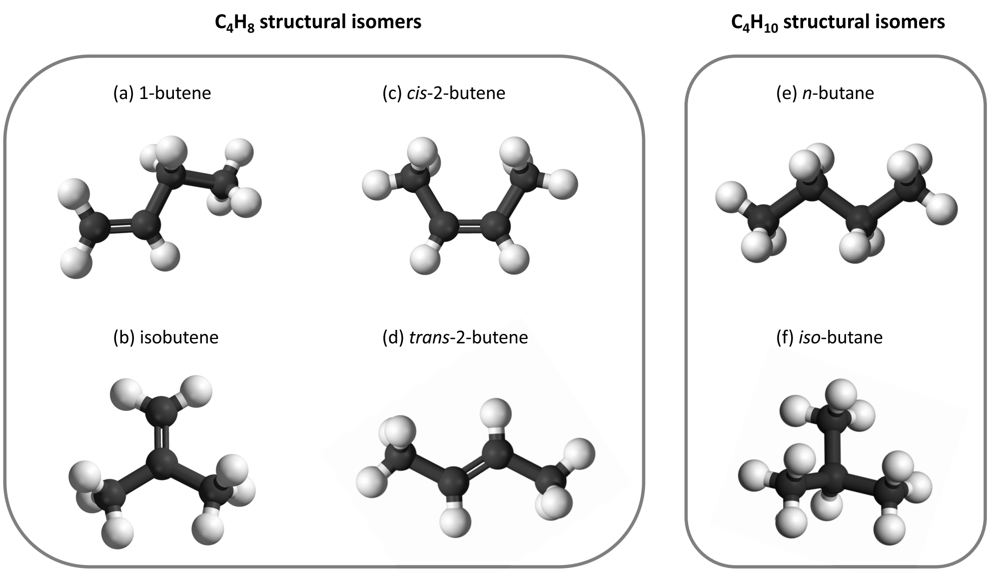

Figure 39. Structural isomers of butene (C_4H_8) and butane (C_4H_{10}), showing that branched chains become possible when four or more carbon atoms are present. Not all possible isomers are shown—additional cyclic forms are also possible (e.g., cyclobutane, C_4H_8).

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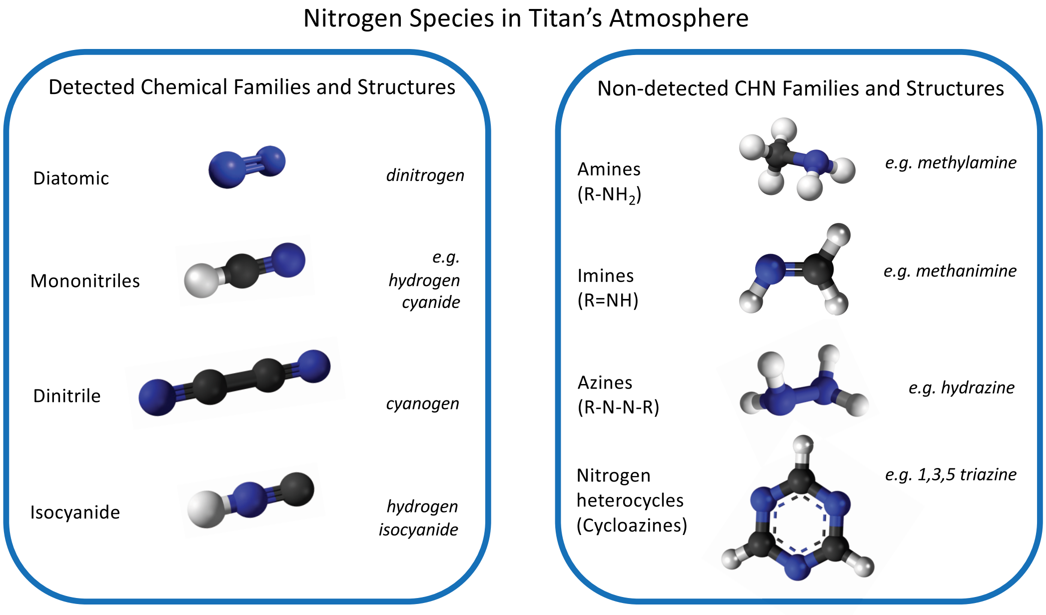

Figure 40. Examples of detected and nondetected nitrogen molecular families in Titan's atmosphere.

$$HC_3N + H^- \rightarrow C_3N^- + H_2 \quad (265)$$

Successively larger aerosol particles are produced through a variety of ion−neutral and ion−ion reactions.[493−495] The largest charged particles tend to be predominantly negative ions, due to their higher mobility.

Loss. Since aromatic rings, once formed, are very stable, with many possibilities to disperse absorbed energy internally, their principal loss channels will be either (a) to form radicals and then larger molecules, (b) to agglomerate, or (c) to condense.

Future Directions. Much work is still required to further elucidate the growth of large particles, especially the relative importance of ion versus neutral chemistry at different altitudes. See also the later section on the topic of PAHs.

■ GAPS IN OUR KNOWLEDGE

In this section we consider where the gaps are in our current knowledge and understanding of Titan's atmospheric composition and chemistry and how these gaps might be addressed in the near future through combinations of astronomy, laboratory, and theoretical work.

Aliphatic Species. *Hydrocarbons.* At present, C_4H_2 remains the only C_4 hydrocarbon species definitively detected in the neutral atmosphere, while no aliphatic C_n species with $n \geq 5$ have been detected (benzene, c-C_6H_6, being detected as a ring).

Some example reactions producing C_4H_x species that are thought to occur include the following:[79,299,496,497]

$$CH_3 + C_3H_3 + M \rightarrow C_4H_6 + M^* \quad (266)$$

$$CH + C_3H_8 \rightarrow C_4H_8 + H \quad (267)$$

$$C_2H_3 + C_2H_5 + M \rightarrow C_4H_8 + M^* \quad (268)$$

Species with four or more carbon atoms show increased possibilities for structural isomerization, as illustrated in Figure 39. This results in both increased challenges for observational detection and new and interesting chemical possibilities such as branched-chain molecules.

Upper limits for *n*-butane and *i*-butane (C_4H_{10}) have been calculated as 5×10^{-7} and 4×10^{-8}, respectively, from CIRS spectra at 200−250 km, 30° N−30° S.[498]

Future Work. Astronomical detection of species such as C_4H_x, x = 4, 6, 8, 10 (i.e., butynes and butenes) and even C_5H_x would greatly help to improve constraints on photochemical models, which are currently lacking in data to model for this regime. Building our knowledge of aliphatic species such as C_4 and C_5 molecules may provide a better understanding of the pathways to benzene or other cyclic species.

In parallel, photochemical models that currently treat multiple isomers under single formulas such as C_4H_8 and C_4H_{10} must continue to expand treatment of separate isomers. To date this has been sparse and primarily for a few specific cases for which isomeric data exist: especially HCN/HNC and CH_2CCH_2/CH_3CCH, which are considered separately in current models.[90,91,99,103] A good reason for lack of inclusion of separate isomers is lack of knowledge of branching ratios and isomer-specific reaction rates. Monte Carlo simulations have proved useful at showing which reaction rate uncertainties have the biggest effects on the uncertainties in the solution.[87,88] These studies thereby provide important prioritization of where resources such as laboratory time and theoretical effort (e.g., TST calculations) can best be spent to most rapidly improve our knowledge.

Nitrogen Species. All of the nine detected nitrogen compounds in Titan's neutral atmosphere, formed from dissociation products of N_2 and CH_4, are triple-bonded. These include N_2 itself and eight known cyanides, which include nitrogen in a terminal −C≡N functional group.

Nitriles (cyanides) appear to be stable and plentiful in Titan's atmosphere, and further examples are sure to be found. In 1985, in the wake of the *Voyager* IRIS discoveries, Cerceau et al.[499] studied the infrared spectra of seven undetected nitriles to facilitate further new detections, and 35 years later, four of these seven species had been detected on Titan (CH_3CN, C_2H_3CN, C_2H_5CN, and CH_3C_3N), although ironically all these detections were made through submillimeter wave astronomy, not infrared

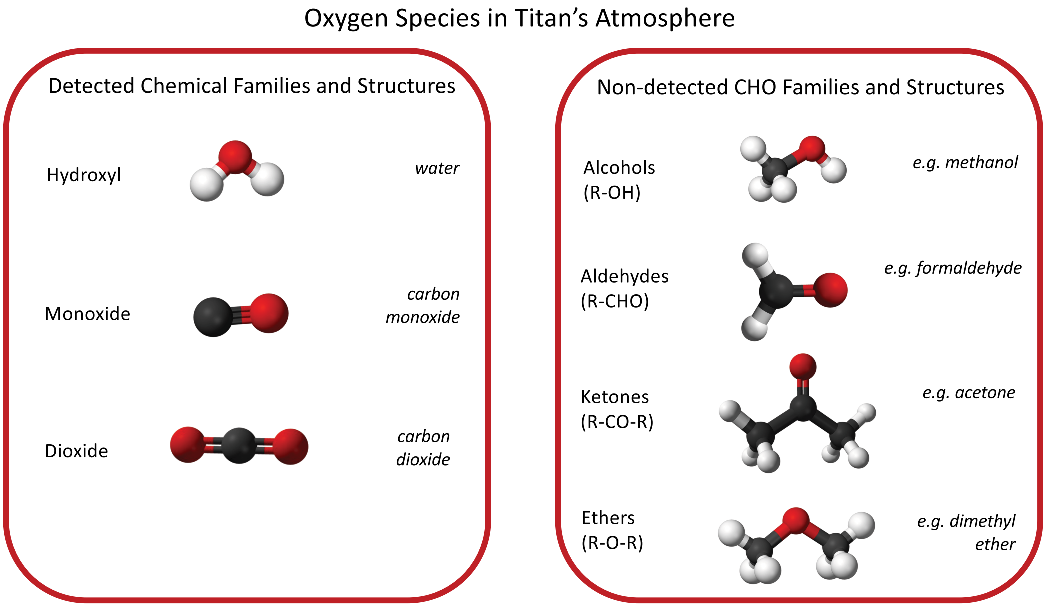

Figure 41. Examples of detected and nondetected oxygen molecular families in Titan's atmosphere.

spectroscopy.[164,166−168] Upper limits for the three remaining undetected species plus one other were calculated by Coustenis et al.:[500]

crotononitrile ($CH_3(CH)_2CN$)	2.5×10^{-7}
butanenitrile ($CH_3(CH_2)_2CN$)	5.0×10^{-7}
isobutyronitrile ($(CH_3)_2CHCN$)	2.0×10^{-7}
cyanocyclopropane ($\Delta{-}CN$)	1.5×10^{-7}

Nitrogen has yet to be detected with other types of bonding (i.e., where it is not in a triple bond), such as in amines, imines (beyond HNC), azines, and nitrogen heterocycles (see Figure 40). A simple example is ammonia (NH_3), which was tentatively inferred from *Cassini*'s mass spectra at high altitudes at mixing fractions of $\sim 3-4 \times 10^{-5}$ but has not yet been uniquely detected due to the barometric degeneracy problem of unit-resolution mass spectroscopy.[219,501]

The major channel for ammonia production is thought to be via NH_2 + H_2CN, as follows:[103]

$$NH + C_2H_4 \rightarrow NH_2 + C_2H_3 \quad (269)$$

$$CH_2NH_2^+ + e^- \rightarrow NH_2 + {}^3CH_2 \quad (270)$$

$$N(^4S) + CH_3 \rightarrow H_2CN + H \quad (271)$$

$$NH_2 + H_2CN \rightarrow NH_3 + HCN \quad (272)$$

Ammonia is mostly lost through photodissociation.

Upper limits for some molecules in the lower atmosphere have been estimated, including 1.3 ppb (3σ) for NH_3 at 107 km, 25° S[502] and 0.35 ppb (3σ) for methanimine (CH_2NH) in the stratosphere.[503]

Future Work. No molecules having both oxygen and nitrogen (e.g., HNO) and more complex amino acids have been detected. Detection of such functional groups and molecules, which are important for biological activity on Earth, is a key area of future research. Several nitriles have been detected only through submillimeter astronomical techniques, as previously mentioned, but not using infrared techniques, despite several decades of attempts.[49,499,500,502] In fact, laboratory line lists with intensities do not exist for many of the nitriles sought in the infrared, except CH_3CN,[504,505] hampering the search and implying a need for new laboratory work to obtain low-temperature spectra.

Oxygen Species. Few oxygen compounds have been detected in Titan's atmosphere: only CO, CO_2, and H_2O to date. Diatomic molecular oxygen, O_2, which is readily found in the atmospheres of the inner planets, is absent, allowing organic chemistry to proceed to great complexity. The oxygen compounds detected appear to be attributable to an external source of oxygen (both O and OH), most likely originating from Enceladus.[57,81] Prior to the discovery of the Enceladus plumes, a meteoritic source was favored,[506] and some meteoritic contribution may still be present.[97]

Other than CO, which is present at a relatively high abundance (~50 ppm[133]), oxygen is a minor although potentially important ingredient of Titan's atmosphere. This is because many molecules of biological importance require oxygen.[507] As early as the 1980s it had already been demonstrated that hydrolysis of Titan tholins ($H_xC_yN_z$) added oxygen to form amino acids of biological relevance,[508] which was subsequently confirmed in many similar experiments. More recently, Hörst et al.[475] showed that even in the gas phase, amino acids may be synthesized in a Titan-like atmosphere when CO is added to mixtures of CH_4 and N_2 in radiofrequency discharge experiments.

Photochemical models[97] predict that trace amounts of molecules such as HNO, HNCO, H_2CO, and CH_3OH should be present in the atmosphere and perhaps detectable at high altitudes by observatories such as ALMA. To date, few published studies have attempted to directly identify further oxygen species. The *Cassini* INMS team published upper limits for methanol (CH_3OH) and acetaldehyde (CH_3CHO) of 30 and 10 ppb, respectively, in the ionosphere at 1100 km.[219] In the stratosphere, upper limits have been determined for methanol and formaldehyde of 6 and 2 ppb, respectively, at 107 km, 25° S[502] from infrared spectroscopy with *Cassini* CIRS.

Future Work. Vibrational (IR) and/or rotational (submillimeter) line lists exist for most small oxygen compounds currently undetected in Titan's atmosphere (see Figure 41), making astronomical searches viable.[509−511]

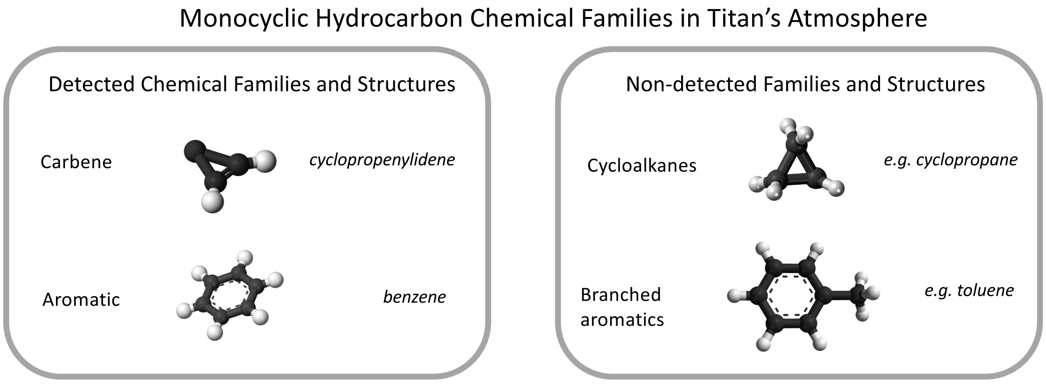

Figure 42. Examples of detected and nondetected monocyclic hydrocarbons in Titan's atmosphere.

Cyclic Molecules. *Single Hydrocarbon Rings.* Two small cyclic molecules have been definitively detected in Titan's neutral atmosphere: cyclopropenylidene (c-C_3H_2)[165] and benzene (c-C_6H_6).[49] Other small cyclic molecules likely to exist include the saturated cycloalkanes—cyclopropane (c-C_3H_6), cyclobutane (c-C_4H_8), and larger—and possibly cycloalkenes such as cyclopropene (c-C_3H_4), cyclobutene (c-C_4H_6), cyclobutadiene (c-C_4H_4), and others. Substituted rings are also possible: cyanocyclopropane (c-C_3H_5CN).

In the ISM, several single-ring molecules have been detected. These include the small three-carbon rings cyclopropenylidene (c-C_3H_2)[306] and its related radical c-C_3H[512] and a substituted species, ethynyl cyclopropenylidene (c-C_3HCCH).[513] The five-sided ring cyclopentadiene (c-C_5H_6) and the six-sided rings benzyne (*o*-C_6H_4) and benzene (c-C_6H_6) have also been detected.[348,513,514]

Future Work. Work is needed on all fronts to advance our understanding of the formation pathways, stability, and prevalence of small cyclic molecules in Titan's atmosphere (see Figure 42). These include astronomical observations, laboratory work, and photochemical modeling. In the 2030s, we anticipate direct in situ measurements of such molecules by the *Dragonfly* probe's *Dragonfly* Mass Spectrometer (DraMS) instrument, which unlike *Cassini* INMS will have the ability to definitively identify molecular structure through a combination of tandem mass spectrometry (MS/MS) and gas chromatography−mass spectrometry (GCMS).[515]

Multiring Hydrocarbons: PAHs and Polyphenyls. PAHs are multiring molecules composed of carbon and hydrogen that exhibit aromatic character, that is to say, they have delocalized π bonding electrons. Example include naphthalene (two fused six-membered rings), indene (one five-sided and one six-sided ring), anthracene and phenanthrene (three six-membered rings), and larger examples (see Figure 43). Benzene is not considered to be a PAH since it has only one ring.

PAHs have long been suspected to exist in interstellar space[516] and have been implicated as culprits responsible for the so-called diffuse interstellar bands (DIBs)[517] (for a review, see ref 518). To date, only a single nonfunctionalized PAH has been uniquely identified in space (indene, C_9H_8[513]), although a greater number of CN-substituted single and double rings (cyano-PAHs) have been identified, assisted by their strong rotational lines due to the cyanide group—see the review by McCarthy and McGuire.[519]

Near-IR emission at 3.28 μm has also been seen in Titan's dayside spectrum by *Cassini* VIMS.[520] In a model by López-Puertas et al.,[521] this emission was attributed to a combination of

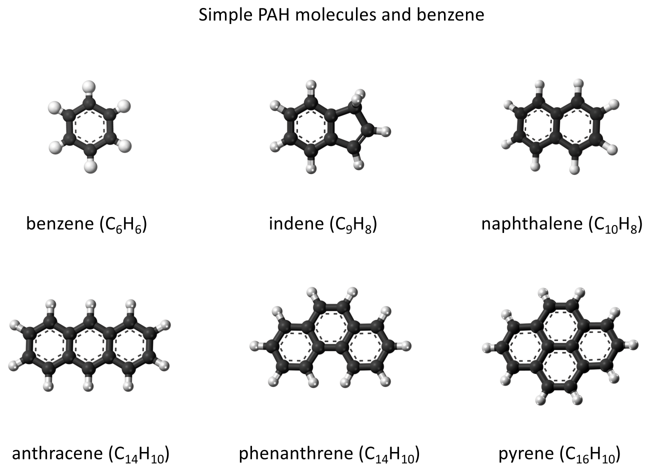

Figure 43. Benzene and polycyclic aromatic hydrocarbon molecules (PAHs). Image credit: individual PAH graphics from Wikimedia Commons.

PAHs with 9−96 carbons (up to 11 fused rings) using laboratory cross sections as measured in the Ames PAH database.[522] However, unique identification of individual PAHs was not possible.

Laboratory experimental work on haze formation by UV photolysis has shown that the inclusion of benzene in initial reagent mixtures along with N_2 and CH_4 leads to the formation of significantly larger molecules than when a N_2/CH_4 mixture is used.[523] More recently, naphthalene has also been used as a starting reagent in lab tholin experiments[524] showing similar results. It should be noted that on Titan both benzene and naphthalene would presumably first have to form from methane, so their use in lab experiments may be considered an acceleration of a natural process that could in principle start from a pure N_2/CH_4 mixture and arrive at the same result over long time periods.

Multiring organic molecules are not constrained to form as fused-ring PAHs such as naphthalene but may instead form as polyphenyls (see Figure 37). It has been argued that a significant amount of carbon rings in Titan's atmosphere may be in the form of polyphenyls rather than fused rings.[525] Titan's aerosols are likely to be a mixture of fused and unfused rings, forming monomers and then fractal aggregates.[526]

Future Work. Future laboratory and eventually in situ experimental work is required to determine the relative importance of fused versus nonfused rings.

Fullerenes. Fullerenes are carbon allotropes formed of rings of five to seven atoms in closed or partially closed mesh structures. These can include buckminsterfullerenes ("buckyballs"), such as the spherical (C_{60}) and ellipsoidal (C_{70}) molecules,[527,528] and also sheets (graphene) and cylinders (carbon nanotubes) (see Figure 44). Despite their large size and apparent complexity, buckyballs have been detected in space both as neutrals[529] and ions[530] and in meteorites.[531] Fullerenes have been hypothesized to exist in Titan's atmosphere,[532] although a recent attempt to detect them in *Spitzer* data proved unsuccessful.[533]

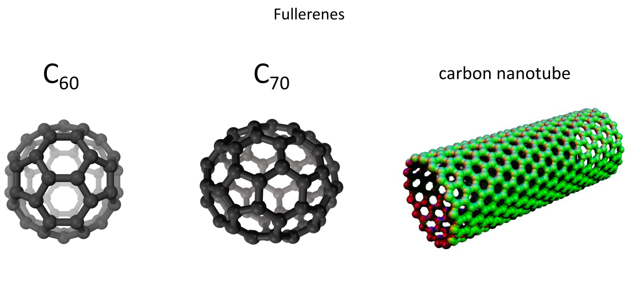

Figure 44. Fullerenes: C_{60}, C_{70}, and carbon nanotube. Image credit: individual graphics from Wikimedia Commons.

Future Work. Greater sensitivity with observatories such as the *James Webb Space Telescope* (JWST)[534] may enable more sensitive searches for fullerenes in Titan's atmosphere. In addition, little lab work has been done at present to determine what effect the presence of fullerenes could have on Titan's atmospheric chemistry, aerosol formation, and surface geology.

PANHs. Nitrogen heterocycles and PANHs are similar to PAHs but with nitrogen incorporation into the ring structure (see Figure 45).[165] Nitrogen heterocycles have been sought unsuccessfully in interstellar space, with upper limits for molecules such as pyridine and quinoline derived.[535] Mass spectroscopy of Titan's atmosphere with *Cassini* INMS has identified peaks at masses that could correspond to N-heterocycles, such as $C_5H_5NH^+$ (could be protonated pyridine) at mass 80 and $C_4H_4N_2H^+$ (possibly protonated pyrimidine) at mass 81.[219] However, aliphatic variants are possible, making the PANH ion identification uncertain.

Recently, Nixon et al.[165] made the first astronomical search for pyridine and pyrimidine in Titan's atmosphere using ALMA and derived upper limits on their disk-averaged (global) abundances: pyridine (c-C_5H_5N) at 1.15 ppb (2σ) above 300 km[165] and similarly pyrimidine (c-$C_4H_4N_2$) at 0.85 ppb (2σ) also above 300 km.

Laboratory work has examined how tholin (Titan haze analog) formation in UV photolysis experiments is affected by the inclusion of N-heterocycles such as pyridine and quinoline.[536,537] Changes in the spectrum show similarities to features in Titan's haze spectrum,[536] and the structures formed show a mixture of polymeric and random copolymeric structures.[524]

Future Work. In the future, more sensitive astronomical searches may be undertaken, for example using ALMA and JWST. Photochemical models at present do not include detailed descriptions of N-heterocycle formation and growth, which must be included in future generations to adequately model processes leading to haze formation.

Sulfur and Phosphorus Chemistry. To date, no compounds of sulfur or phosphorus have been found in Titan's atmosphere. Nixon et al.[538] made the first quantitative assessment of upper limits for the most simple reduced species, PH_3 and H_2S, of 1 and 300 ppb, respectively, in the stratosphere (~250 km). Phosphine gas has even been mooted as a biosignature gas in planetary atmospheres,[539] although this conclusion has been debated.[540] A sensitive search for CS was made by Teanby et al.[503] with ALMA, yielding an upper limit of either 7.4 ppt (uniform profile above 100 km) or 25.6 ppt (uniform profile above 200 km).

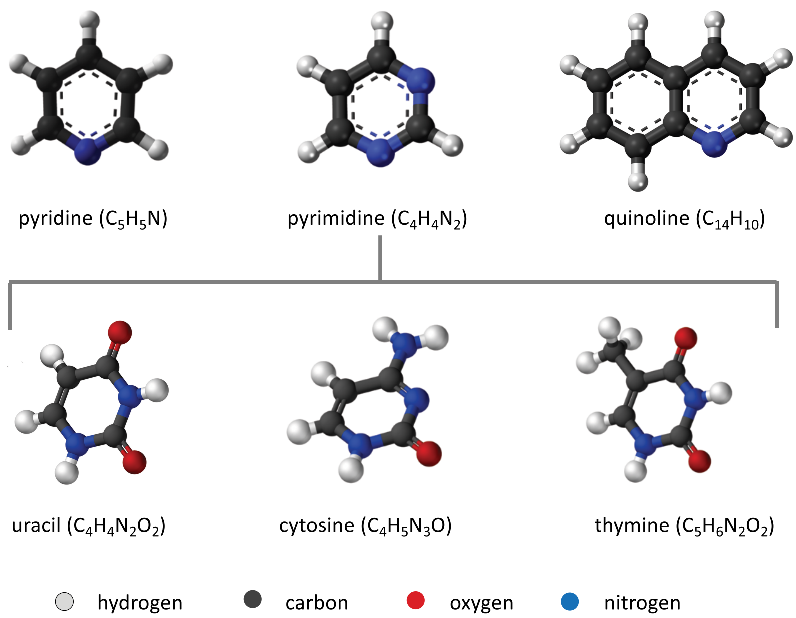

Figure 45. Nitrogen heterocycles and polycyclic aromatic nitrogen heterocycles (PANHs). Top row: simpler N-heterocycles with one or two rings and one or two nitrogen atoms incorporated. The importance of the search for pyrimidine is illustrated by the bottom row: pyrimidine forms the backbone ring for two of the four nucleobases in DNA (cytosine and thymine) and one in RNA (uracil). Image credit: individual PAH graphics from Wikimedia Commons.

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The first (and so far only) photochemical model to include sulfur chemistry was published by Hickson et al.[541] and predicts that CS and H_2CS should be the most abundant sulfur-bearing species in the upper atmosphere, transitioning to C_3S, H_2S, and CH_3SH in the lower atmosphere. However, in the absence of constraints, predictions remain highly uncertain.

In principle, the O/S ratio should allow further constraint of the source of Titan's oxygen flux, since the O/S ratio is predicted to be some 1000× less for a cometary source (O/S ∼ 100)[542] than an Enceladus source (O/S ∼ 10^5).[543] Detection of sulfur in Titan's atmosphere may also provide evidence for cryovolcanic activity.[252]

Both phosphorus and sulfur are among the six most essential elements for biochemistry on Earth (the so-called CHNOPS elements). With four of the six already detected on Titan, it is therefore of considerable interest to seek the remaining two, to further assess Titan's potential for astrobiology. Recent reports that all six CHNOPS elements have now been detected in the plume material of Enceladus[543,544] make it feasible that some trace amounts of P and S arrive at the top of Titan's atmosphere, as is the case apparently with O.[57]

Future Work. Future work is required on both the direct detection of P- and S-containing substances by both astronomical and in situ techniques and also in laboratory work, computer photochemical modeling, and clarification of reaction pathways and rates, especially at low temperatures.

Radicals. For completeness, we include consideration of radical species—atoms and molecules with unpaired free electrons—even though these are highly reactive and unlikely to be found in significant numbers or significantly deep in Titan's neutral atmosphere. Radicals include fragments of CH_4, such as CH (methylidene), CH_2 (methylene), and CH_3 (methyl), as well as ground-state and excited nitrogen atoms formed from breakup of N_2, such as as $N(^2D)$ and $N(^4S)$.

Many radicals (CN, OH, etc.) have been observed in the ISM,[450] including at least one cyclic radical (c-C_3H),[512] and also in comets[545] and tenuous satellite exospheres.[546] However, to date only the methyl radical has been detected by astronomical techniques in a planetary atmosphere.[547,548]

Future Work. ALMA observations are particularly sensitive to Titan's upper atmosphere and can sense HCN at altitudes of up to 1200 km.[128,159] Future investigations with ALMA may allow the detection of radicals with dipoles, and more sensitive infrared observatories such as JWST may prove effective at detecting radicals such as methyl in the infrared.[534]

CONCLUSIONS

The organic-rich atmosphere of Titan constitutes the most complex atmospheric chemical network known outside of Earth. This provides a unique natural laboratory for understanding the synthesis of organic compounds, processes that may have been important early in the history of the Solar System[549,550] and may have seeded the origins of life on Earth.[551,552]

Therefore, it is of substantial scientific importance to better understand these processes and chemical results. This field of inquiry brings together astronomers, laboratory chemists, theoretical chemists, and atmospheric modelers whose combined approaches are needed to unravel the entire picture. Substantial progress has been made, especially stimulated by the recent wealth of data from the *Cassini*−*Huygens* mission[2,3] and the selection of the *Dragonfly* mission[275] that will arrive in the 2030s.

Astronomy. Titan is a distant object, and gathering robust information is difficult in the absence of spacecraft: astronomy is currently the only means to gather data about Titan directly. Currently active ground- and space-based observatories such ALMA, IRTF, and JWST are providing continuity of data collection since the end of *Cassini*−*Huygens* regarding seasonal changes in Titan's atmosphere[147,159] and new information on the chemistry, composition, and isotopic ratios.[133,165,166,168,170,171,325,553,554]

Laboratory Studies. While data collection through astronomy and remote sensing continues, a robust campaign of laboratory experiments and theoretical work is continuing in parallel to understand the origins and chemical evolution of the atmosphere and interaction with the surface and subsurface. These diverse inquiries include spectroscopy of gases,[341,498,555−563] measurement of reaction rates,[242,347,354,358,409,564−568] and experimental work on cocrystals,[276,277,297,417,569,570] ices,[571−582] and hazes (tholins).[110,111,583−592]

Modeling. The chemistry of Titan's atmosphere cannot proceed without disturbing the medium in which it takes place: the minor gases and haze generated have a substantial effect on the heating and cooling of the atmosphere,[593] and in turn, changes to the thermal structure of the atmosphere lead to dynamical motions, including vertical eddy mixing and meridional transport. As gases are transported, they enter atmospheric regions that may have greater or lesser photon flux from the Sun, have fewer or greater opportunities to interact with electrons, and encounter differing densities of radicals and other reagents. Therefore, decoupling chemistry from dynamics is not possible. Combining the current generation of global circulation models (GCMs)[155,594−598] and photochemical models[99,100,102,103,599] to create 2D and 3D coupled chemical-GCMs is a challenging but important task that must occupy the next generation of modelers.

Future Missions. The *Dragonfly* mission, estimated to land on Titan in ∼2034, will provide a wealth of new data about Titan's surface and atmospheric boundary layer. However, *Dragonfly* will only investigate the low latitudes, including dunes and the crater Selk. In the future, an orbiter, as envisaged by several published studies,[600−602] would provide the important benefit of a truly global picture, including potentially complete global mapping of the atmosphere and surface at uniform resolution, with time-domain information to search for changes occurring. Other elements, such as a balloon, airplane, and/or floating lake probe, could provide valuable in situ information about other environs.[603−605]

There is no doubt that Titan still offers many challenges to our understanding that will provide fertile areas of study for future generations of scientists[21,606] and offer rewards through important insights into the chemical evolution of the Solar System and origins of life in the universe.

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Notes

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ACRONYMS AND ABBREVIATIONS

ALMA Atacama Large Millimeter/submillimeter Array
CAPS *Cassini* Plasma Spectrometer
CDA Cosmic Dust Analyzer (*Cassini* instrument)
CIRS Composite Infrared Spectrometer (*Cassini* instrument)
DR dissociative recombination
DSMC direct simulation Monte Carlo
ESA European Space Agency
GCM global circulation model
GCMS Gas Chromatograph/Mass Spectrometer (*Huygens* instrument)
HASI Huygens Atmospheric Structure Instrument
INMS Ion and Neutral Mass Spectrometer (*Cassini* instrument)
IRAM Institut de Radioastronomie Millimetrique
IRIS Infrared Interferometer Spectrometer (*Voyager* instrument)
IRTF *Infrared Telescope Facility*
ISM interstellar medium
ISO *Infrared Space Observatory*
IUPAC International Union of Pure and Applied Chemistry
JWST *James Webb Space Telescope*
LTE local thermodynamic equilibrium
NASA National Aeronautics and Space Administration
PAH polyaromatic hydrocarbon
PANH polyaromatic nitrogen heterocycle
RPWS Radio and Plasma Wave Spectrometer (*Cassini* instrument)
RSS Radio Science Subsystem (*Cassini* instrument)
SNR signal to noise ratio
TEXES Texas Echelon Cross Echelle Spectrograph
TMC Taurus Molecular Cloud
TST transition state theory
UVIS Ultraviolet Imaging Spectrometer (*Cassini* instrument)
VIMS Visible and Infrared Mapping Spectrometer (*Cassini* instrument)
VMR volume mixing ratio

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