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Updated Polyyne Chemistry for Polyyne Polymerization and Organic Aerosol Synthesis in the Atmosphere of Titan

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Abstract

For the last four decades, the role of polyynes such as diacetylene and triacetylene in the chemical evolution of the atmosphere of Saturn's moon Titan has been a subject of vigorous research. These polyacetylenes are thought to serve as an ultraviolet radiation shield in planetary environments thus acting as prebiotic ozone and are considered as important constituents of the visible haze layers on Titan. However, the underlying chemical processes which initiate the formation and control the growth of polyynes have been the least understood to date. Here we present preliminary results of including postulated chemistry into a photochemical model for Titan. The insertion reactions exhibit no entrance barrier, are exothermic, and all transition states, which are involved, are below the energy of the reactant molecules. Due to these characteristics, the elementary reaction of the ethynyl radical with diacetylene represents an efficient pathway to produce triacetylene in Titan's atmosphere in those regions where density profiles of photolytically generated ethynyl radicals and diacetylene overlap. Our models of Titan's atmosphere indicate that successive reactions of the triacetylene molecule can yield even more complex polyynes. Here, ethynyl radicals (CCH) or 1,4-butadiynyl radicals (HCCCC), formed via photodissociation of acetylene and diacetylene, respectively, can react with triacetylene to tetraacetylene (C_8H_2) and pentaacetylene ($C_{10}H_2$), respectively. This offers important sinks for triacetylene and produces potential polyyne precursors for the organic aerosol layers.

1. Introduction

The implementation of the reaction of ethynyl radicals with diacetylene into a photochemical model of Titan's atmosphere requires two input parameters: the reaction products, i.e. triacetylene plus atomic hydrogen, and rate constants. Due to the absence of any experimental data, we incorporated computed rate constants of $1.5 \pm 0.5 \times 10^{-10}$ cm^3s^{-1} to form triacetylene plus atomic hydrogen into the model. Over the temperature range of 94 K to 200 K, the rate constants are temperature independent. This finding is characteristic of an exoergic reaction which has no entrance barrier and which is dictated by attractive, long-range forces. Our models suggest that polyynes of the generic formula $C_{2n}H_2$, ($n \geqq 2$) can be readily formed in the atmosphere of Titan via reactions of ethynyl (C_2H) and 1,3-butadiynyl radicals (C_4H) with (poly)acetylene molecules ($C_{2n}H_2$) such as acetylene, diacetylene, and triacetylene. This possibility was first pointed out by Allen et al. (1). The mechanisms consist of two steps: the photolysis of the radical precursor like acetylene and diacetylene and a propagation of the long-chain polyyne leading effectively to a polyyne extension plus two hydrogen atoms with n = 1, 2, 3…; C_2H and C_2H_2 are the essential building blocks for polyynes. The propagation of the chain is facilitated and enhanced by two factors: the lack of reaction barriers such as discussed in this paper, and the low abundance of hydrogen because of Titan's low gravity which allows hydrogen to escape readily. Quantitatively spoken, the photochemical models (we terminate the hydrocarbon chain at C_8H_3) predict abundances relative to acetylene of $[C_4H_2]/[C_2H_2]$, $[C_6H_2]/[C_2H_2]$, and $[C_8H_2]/[C_2H_2]$ to be about 10^{-2}. This model nicely simulates the abundances of diacetylene and acetylene in the neutral region of the atmosphere as observed by Cassini-Huygens probe (2, 3). The production of the polyynes is significant throughout the entire atmosphere because higher order polyynes such as diacetylene are photodissociated mainly by ultraviolet photons with wavelengths between ~120 nm and ~250 nm, where there is no or little shielding by H_2, N_2, or CH_4. As the rate constants for C_4H_2 and C_6H_2 photolysis and that for $C_{2n}H_2$ polymerization are similar, the vertical profiles of C_4H_2 and C_6H_2 are

similar. The larger abundance of C_8H_2 than C_4H_2 and C_6H_2 is due to smaller photolysis rate constant for C_8H_2. Above ~800 km (homopause), their mixing ratios are affected by molecular diffusion. The chemical schemes can be summarized as follows, with n = 1, 2, 3, ...

$C_2H_2 + h\nu \rightarrow C_2H + H$

$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H$

$C_2H_2 + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + 2H$

$C_4H_2 + h\nu \rightarrow C_4H + H$

$C_4H + C_{2n}H_2 \rightarrow C_{2n+4}H_2 + H$

$C_4H_2 + C_{2n}H_2 \rightarrow C_{2n+4}H_2 + 2H$

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