Astrochemistry: Recent Successes and Current Challenges
Poster Book IAU Symposium No. 231, 2005
A. J. Markwick-Kemper, ed.

DOI: 00.0000/X000000000000000X

Laboratory Study of the Atmospheres of Outer Planets and Titan: Gas Phase Kinetics of C_2H Reactions at Low Temperature

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Abstract.

Photochemistry of acetylene (C_2H_2) and the subsequent reactions of the ethynyl radical (C_2H) have been shown to play an important role in the formation of complex organic molecules in planetary atmospheres and especially in Titan's atmosphere. There have been relatively few kinetic investigations of reactions with the ethynyl radical at low Temperature (down to 70 K) because of their experimental difficulty. We have developed (Lee et al. 2000) a pulsed Laval apparatus coupled to a time-of-flight mass spectrometer to study experimentally the gas phase chemistry (reaction kinetics and product distributions) of the C_2H radical with several molecules involved in Titan's Atmosphere.

This apparatus generates a pulsed and uniform low temperature gas flow down to 70 K. Radiation from a 193 nm pulsed laser is used to generate the C_2H radical coaxially down the length of the expansion by photolysis of acetylene. The reaction kinetics is followed in the flow by measuring the chemiluminescence of excited $CH(A^2\Sigma)$ formed in the reaction of C_2H with O_2. Our experiment has provided new kinetic rate coefficients for the C_2H radical with four-carbon-atom neutral hydrocarbons (isobutane, 1-butene, isobutylene and 1,3-butadiene). These reactions are rapid (a rate coefficient greater than 1×10^{-10} cm^3 s^{-1} at 104 K) and will soon be included into atmospheric models. Studies of the kinetics of reactions of the ethynyl radical with nitrogen-containing species (CH_3CN, C_2H_5CN and C_3H_7CN) in Titan's atmospheric temperature range (Nizamov & Leone 2004a, Nizamov & Leone 2004b) indicate that the rate coefficients decrease monotonically as the temperature is lowered. The rate constant is small relative to the rate constants for C_2H reactions with more abundant hydrocarbons, indicating that those reactions with nitrogen-containing species account for a very small fraction of the C_2H removal by chemical reactions. Studies of the isotopic effects on the $C_2H + NH_3/ND_3$, $C_2H/C_2D + O_2$ and $C_2H/C_2D + C_2H_2/C_2D_2$ reactions were performed. Those results show a large kinetic isotope effect only for the reaction with NH_3, confirming that the hydrogen abstraction channel is one of the possible mechanisms for this reaction. The study of expensive gases like deuterated species is permitted due to the very small gas quantities used during the pulsed injection of gas.

New experiments will provide important information about the first chemical step in Titan's haze formation: in atmospheric models the reaction of benzene with ethynyl radical is one of the ways of promoting the propagation of PAH formation (Wilson & Atreya 2003). This reaction is studied in our experiment down to 100 K. The detection of the products is allowed for the first time at such low temperatures by sampling the gas stream and using a 118 nm ionization laser and time-of-flight mass spectrometer.

Keywords. astrochemistry, molecular processes, methods: laboratory, planets and satellites: Jupiter, Saturn, Titan.

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