Laboratory Astrophysics: from Observations to Interpretation
Proceedings IAU Symposium No. 350, 2019
F. Salama & H. Linnartz, eds.
doi:10.1017/S1743921319009578

Photochemistry vs. radiation chemistry of cosmic ice analogs

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Abstract. While gas-phase reactions and surface reactions on bare carbonaceous or siliceous dust grains contribute to cosmic chemistry, the energetic processing of cosmic ices via photochemistry and radiation chemistry is thought to be the dominant mechanism for the cosmic synthesis of prebiotic molecules. Because most previous laboratory astrochemical studies have used light sources that produce $>$ 10 eV photons and are, therefore, capable of ionizing cosmic ice analogs, discerning the role of photochemistry vs. radiation chemistry in astrochemistry is challenging. By using a source whose photon energy does not exceed 8 eV, we have studied ammonia and methanol cosmic ice reactions attributable solely to photochemistry. We compare these results to those obtained in the same ultrahigh vacuum chamber with 1 keV electrons which instead initiate radiation chemistry in cosmic ice analogs.

Keywords. Astrochemistry, radiation mechanisms: non-thermal, cosmic rays, ISM: molecules

1. Introduction

The energetic processing of ices surrounding interstellar dust grains can be broadly categorized as either radiation chemistry or photochemistry (Arumainayagam *et al.* 2019). Radiation chemistry involves ionizing radiation, which, in cosmic chemistry, includes high-energy particles (e.g., cosmic rays consisting mostly of protons) and high-energy photons (e.g., extreme-UV (12.4-124 eV), X-rays, and γ-rays). Exclusive to radiation chemistry are 1) the production of low-energy ($<$ 20 eV) secondary electrons that are responsible for the majority of radiation chemistry effects, 2) non-uniform distribution of intermediates, and 3) multiple reaction products due to non-specific chemistry (Boyer *et al.* 2016). Also, unlike photochemistry, radiation chemistry is not subject to electron spin conservation rules. In contrast to radiation chemistry, photochemistry is defined as chemical changes resulting from photon-induced electronic excitation not involving ionization. Therefore, vacuum-UV (6.2-12.4 eV) light may initiate radiation chemistry as well as photochemistry because the threshold for producing low-energy electrons in condensed matter is lower than the gas phase ionization energy for a given molecule. For example, photoelectric emission threshold of amorphous water ice (the main constituent of cosmic ices) is $\sim$ 10.2 eV, which is smaller than the ionization energy of 12.6 eV for gas-phase water. This shift must be carefully considered when conducting laboratory photochemistry studies of cosmic ice analogs (Mullikin *et al.* 2018). For example, microwave discharge hydrogen flow lamp emissions are dominated by the Lyman-alpha line at 10.2 eV, which can ionize common cosmic ice constituents such as condensed water, ammonia, and methanol. Discriminating between radiation chemistry and photochemistry is essential for the prediction of the molecules produced in the interstellar medium, their abundances, and their formation pathways.

2. Overview

The setup at Wellesley College is equipped to perform both photochemistry and radiation chemistry studies within the same chamber, allowing for direct comparison between the two processes. A Ta(110) single crystal, located within a chamber kept at a pressure of $\sim 2 \times 10^{-9}$ torr, is cooled by liquid nitrogen to ~ 90 K. Single-component cosmic ice analogs of known thicknesses are grown on the cooled crystal and irradiated with < 7.4 eV photons from a laser-driven photon source, simulating photochemistry, or with low-energy (7 - 10 eV) or high-energy (1 keV) electrons, simulating the effects of radiation chemistry. After irradiation, the crystal is radiatively heated to cause desorption of products, which are monitored by a quadrupole mass spectrometer. Our results demonstrate that both radiation chemistry and photochemistry of condensed ammonia produce hydrazine (N_2H_4), diazene (N_2H_2), triazane (N_3H_5), and one or more isomers of N_3H_3 (Mullikin *et al.* 2018; Shulenberger *et al.* 2019). Semiquantitative trends in the dependence of product yield on film thickness and radiation fluence indicate that the formation mechanism for both hydrazine and diazene involve radical-radical reactions (of amidogen ($\bullet NH_2$) and imidogen ($\bullet NH$) radicals, respectively). Photochemistry studies of methanol show the production of methoxymethanol (CH_3OCH_2OH), ethylene glycol ($HO(CH_2)_2OH$), and dimethyl ether (CH_3OCH_3), which are known radiation chemical products (Schneider *et al.* 2019). One proposed formation mechanism for methoxymethanol is the radical-radical reaction of the hydroxymethyl ($\bullet CH_2OH$) and methoxy ($CH_3O\bullet$) radicals.

3. Implications

Despite the intrinsic differences between photochemistry and radiation chemistry, our studies to date of methanol and ammonia have not detected differences in the identities of the photolysis and radiolysis products. These preliminary results suggest that there may be a shared mechanism involving electronic excitation, dissociation, and subsequent radical recombination. Additional quantitative experiments are needed to determine effective cross sections and branching ratios for each product; such information can be incorporated into astrochemical models for more accurate predictions of interstellar molecule abundances. In cosmic ices, there may also be a difference in flux of secondary electrons-agents of radiation chemistry-and low-energy photons-instigators of photochemistry. Photons produced via excitation of gaseous hydrogen within dense molecular clouds have a flux of $\sim 10^3$ photons cm^{-2} s^{-1} (Prasad & Tarafdar (1983)), whereas our preliminary calculations indicate fluxes as high as $\sim 3 \times e^3$ electrons cm^{-2} s^{-1} for secondary electrons produced in interstellar ices due to incident cosmic rays. These order-of-magnitude calculations suggest that the effects of electrons are at least as important as those of photons in the interstellar synthesis of prebiotic molecules.

This work was supported by grants from the National Science Foundation (NSF grant number CHE-1465161) and Wellesley College (Faculty awards and Brachman Hoffman small grants).

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https://doi.org/10.1017/S1743921319009578 Published online by Cambridge University Press