CH_3CN complex with water as a precursor for radiation induced synthesis of acetamide in low-temperature matrix

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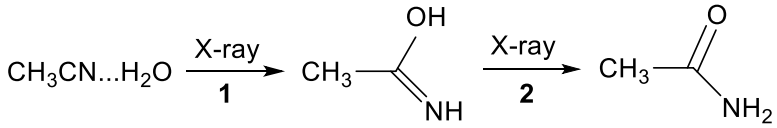
Small nitrogen-containing molecules play an important role in extraterrestrial prebiotic chemistry. In particular, acetonitrile (CH_3CN) was found in different space objects.[1] It is supposed to be a precursor of a variety of biologically relevant molecules, including amino acids [2]. Considering the solid-phase chemistry driven by ionizing radiation, one may come to an idea that the intermolecular complexes of acetonitrile with oxygen-bearing molecules can serve as "building blocks" for complex organic molecules (COMs) containing both N and O atoms. However, little is known on the mechanisms of such processes. The strategy to investigation of the radiation-chemical transformations occurring within isolated complexes frozen in rigid environment was recently developed in our laboratory.[3,4] In this work we have examined for the first time the radiation-induced transformations of acetonitrile complexes with the most common space molecules (water and carbon dioxide) occurring under X-ray irradiation in solid argon matrices at 5 – 6 K using FTIR spectroscopy.

As a first step, the 1 : 1 complex of acetonitrile with water in two conformationals was experimentally obtained by condensation of the ternary gaseous mixtures (CH_3CN/H_2O/Ar) and characterized on the basis of comparison with available computational data.[5] Then, it was shown that the radiolysis of complexes with X-rays led to formation of oxygen-containing COMs, such as acetamide, acetamidic acid, hydroxyacetonitrile and acetonitrile N-oxide. The formation of these products was also confirmed by experiments with isotopic substitution (CD_3CN). Remarkably, the built-up kinetic curves demonstrated induction period for acetamide and maximum for acetimidic acid, which may indicate a new two-step route to the cold radiation-induced synthesis of this important prebiotic molecule in the space environment. Comparison between direct and reverse process shown earlier[6] is discussed and astrochemical implications of the results are outlined.



Scheme 1. Formation of acetamide via radiation-induced assemble in acetonitrile-water complex (**1**) and intermolecular rearrangement (**2**)

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Acknowledgments: This work was financially supported by the Russian Science Foundation (project no. 21–13–00195).