The Radiation Chemistry of $NH_3\cdots CO$ Complex in Cryogenic Media as Studied by Matrix Isolation

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The NH_3/CO system is supposed to be of high significance for cold synthetic astrochemistry leading to the formation of complex organic molecules and prebiotic species.[1–3] The matrix isolation technique is a useful tool for the simulation of primary synthetic processes induced in solids by radiation and light where the matrix-isolated 1:1 intermolecular complexes serving as the simplest "building blocks". In the present work,[4] we have studied the radiation-induced transformations of the $NH_3\cdots CO$ complex in Ar, Kr, and Xe matrices using FTIR spectroscopy.

Matrix samples were obtained by deposition of gaseous mixtures (NH_3/CO/Ng 1/3/1000; Ng = Ar, Kr, or Xe) onto a cold KBr substrate mounted in a closed-cycle helium cryostat. The conditions of the deposition procedure were optimized to obtain a sufficient amount of the target 1:1 $NH_3\cdots CO$ complex. The deposited matrices were irradiated with X-rays (effective energy ca. 20 keV) to different doses (up to 530 kGy) at 6 K. The radiation-induced products and intermediates were characterized by FTIR spectroscopy. The structures, energetics, and IR parameters for the $NH_3\cdots CO$ complex were calculated at the CCSD(T) level of theory. VUV photolysis was performed using a MDHL (microwave-discharged hydrogen-flow) lamp.

Comparison of the FTIR spectra of the non-irradiated samples with the CCSD(T)/L2a_3 calculations demonstrates that the $NH_3\cdots CO$ complex has the configuration with hydrogen bonding through a carbon atom of CO. It was found that the irradiation of the initial complex with X-rays at 6 K leads to the formation of a number of synthetic products, namely HNCO (in all matrices), NH_2CHO (formamide), $NH_2CO^{\bullet}$, and $HNCO{-}H_2$ (in argon and krypton). The matrix effect on the product distribution was explained by the involvement of different excited states of the complex in their formation. It was suggested that formamide results from the singlet excited states of the parent complex while other species mainly originate from triplet ones. $NCO^{\bullet}$, $CN^{\bullet}$, and $NO^{\bullet}$ were found as minor secondary products at high adsorbed doses. Comparison of the radiolysis results with the preliminary data on the VUV photolysis of the matrix-isolated $NH_3\cdots CO$ complex is discussed. Astrochemical implications of the obtained findings are highlighted.

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