Radiation-induced formation of formic acid in the H2O–CO system: a matrix-isolation study

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Abstract

Formation of complex organic molecules under astrophysically relevant conditions is a basically important problem widely addressed in the laboratory simulations. Water and carbon monoxide are among the most abundant molecules in the astrophysical ices, thus the radiation-induced chemistry in the H2O–CO system is of significant interest for astrochemistry. It has been shown previously [1] that irradiation of the frozen H2O/CO mixtures may lead to the formation of formic acid (HCOOH). In the present work, we investigated the radiation-chemical evolution of the H2O–CO molecular system using the matrix-isolation technique, which provides versatile information on both formation and low-temperature reactions of the radiation-induced intermediates.
H2O/CO/Ng mixtures (Ng = Ar, Kr, or Xe; typical concentration is 1/1/1000) were deposited onto a cold (15–25 K) KBr substrate mounted in a closed-cycle helium cryostat. Prepared matrices, containing significant amounts of the H2O–CO 1:1 intermolecular complexes, were cooled down to 5 K, irradiated with X-rays (energy ca. 20 keV), and then annealed stepwise at various temperatures (up to 45 K). FTIR spectroscopy was used to monitor the formation and decay of different species.

Radiolysis of the H2O–CO complexes leads to the loss of H-atoms yielding the OH–CO complexes and some amount of *trans*-HOCO radicals (the less stable *cis*-HOCO conformer is not observed in the noble-gas matrices) [2]. The radiation-induced H-atoms are stabilized at 5 K and could be mobilized by subsequent matrix annealing to react with other matrix-isolated species (for example, H + CO → HCO). Another thermally-induced reaction observed in the studied system is transformation of the OH–CO complexes to the *trans*-HOCO radicals. In Ar and Kr matrices, both the OH–CO → *trans*-HOCO reaction and reactions of H-atoms occur within the same temperature range (25–35 K). In the case of Xe matrices, annealing at 35 K results in complete transformation of OH–CO to *trans*-HOCO, whereas H-atoms mobility is activated at higher temperatures. Formation of HCOOH (detected by the characteristic IR absorptions) was observed in Xe matrices upon annealing at 40–45 K, which evidences the H + *trans*-HOCO → HCOOH reaction. We suggest that this reaction pathway could be more favorable than the H + OH–CO → OH–HCO → HCOOH reaction since formation of HCOOH is not observed in Ar and Kr matrices (where the latter process may happen because H-atoms are reacting at the temperatures low enough, when the OH–CO complex can survive).

To sum up, this work provides some insight into the possible mechanisms responsible for

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the formation of formic acid in the astrophysical ices. We also believe, that similar experimental approach could be applied in model astrochemical studies related to other prebiotic molecules. The work was supported by the Russian Science Foundation (grant 14-13-01266).

References.

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