

Radiation-induced transformations of acetaldehyde molecules at cryogenic temperatures: a matrix isolation study

Pavel V. Zasimov¹, Elizaveta V. Sanochkina¹, Vladimir I. Feldman¹

¹ Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia, 119991
bulgacov2012@yandex.ru

Acetaldehyde is one of the key small organic molecules involved in astrochemical and atmospheric processes occurring under the action of ionizing and UV radiation [1]. While the UV photochemistry of acetaldehyde is well studied [2], little is known about the mechanism of processes induced by high-energy radiation. In this study, we performed the first systematic study on the chemical transformations of CH₃CHO molecules resulting from X-ray irradiation under the conditions of matrix isolation in different solid noble gases (Ne, Ar, Kr, and Xe) at 5 K.

Matrix samples were obtained by deposition of gaseous mixtures (CH₃CHO/Ng or CD₃CDO/Ng 1/1000; Ng = Ne, Ar, Kr, or Xe) onto a cold KBr substrate mounted in a closed-cycle helium cryostat. The deposition temperatures were typically about 8, 18, 25 and 33 K for Ne, Ar, Kr and Xe matrices, respectively. The deposited matrices were irradiated with X-rays (45 kV_p, anode current 80 mA, effective energy ca. 20 keV) to different doses (up to 111 kGy) at 5 K. Photolysis of the irradiated samples was performed using appropriate ARPL-STAR-3W LEDs ($\lambda_D = 620$ nm and $\lambda_D = 520$ nm). The radiation-induced products and intermediates were characterized by FTIR spectroscopy.

The results of this study [3] demonstrate that CO, CH₄, H₂CCO, H₂CCO–H₂, C₂H₂···H₂O, CH₂CHOH, CH₃CO[•], CH₃[•], HCCO[•], and CCO are the main acetaldehyde radiolysis products. It was found that the dominant pathway of acetaldehyde degradation involves C–C bond cleavage leading to the formation of carbon monoxide and methane. The second important channel is dehydrogenation resulting in the formation of ketene, a potentially highly reactive species. The significant effect of the matrix media both on the decomposition efficiency and distribution of the reaction channels was observed. Based on these observations, it was suggested that the formation of the methyl radical as well as vinyl alcohol and the C₂H₂···H₂O complex presumably included a significant contribution of ionic pathways. The decomposition of acetyl radicals under photolysis with visible light leading to the CH₃[•]–CO radical-molecule pair was detected in all matrices, while the recovery of CH₃CO[•] in the dark at 5 K was found only in Xe. This finding represents a prominent example of matrix-dependent chemical dynamics, which may involve the tunnelling mechanism. Probable mechanisms of acetaldehyde radiolysis and their implications for astrochemistry, atmospheric chemistry and low-temperature chemistry are discussed.

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

References

1. C.J. Bennett, C.S. Jamieson, Y. Osamura, R.I. Kaiser, *ApJ* **2005**, 624, 1097.
2. A. W. Harrison et al., *Phys. Chem. Chem. Phys.* **2019**, 21, 14284 and references therein.
3. P.V. Zasimov, E.V. Sanochkina, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2022**, 24, 419.