

Formation and Evolution of $\text{H}_2\text{C}_3\text{O}^{+\bullet}$ Radical Cations: A Computational and Matrix Isolation Study

Zasimov, P.V.,^{1*} Tyurin, D.A.,¹ Ryazantsev, S.V.,^{2,1} Feldman, V.I.¹

*presenter

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

² Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, 121205 Moscow, Russia

The family of isomeric $\text{H}_2\text{C}_3\text{O}^{+\bullet}$ radical cations is of great interest for physical organic chemistry and chemistry occurring in the extraterrestrial media.^{1,2} In this work, we have experimentally examined a unique synthetic route to the generation of $\text{H}_2\text{C}_3\text{O}^{+\bullet}$ from the $\text{C}_2\text{H}_2\cdots\text{CO}$ intermolecular complex and also considered the relative stability and monomolecular transformations of the $\text{H}_2\text{C}_3\text{O}^{+\bullet}$ isomers through high-level ab initio calculations.

Matrix samples were obtained by deposition of gaseous mixtures ($\text{C}_2\text{H}_2/\text{CO}/\text{Ng}$ 1/3/1000; Ng = Ar, Kr, 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 precursor 1:1 $\text{C}_2\text{H}_2\cdots\text{CO}$ complex. The deposited matrices were irradiated with X-rays (effective energy ca. 20 keV) to different doses (up to 200 kGy) at 5 K. Photolysis of the irradiated samples was performed using appropriate LEDs ($\lambda_{\text{D}} = 465$ nm and $\lambda_{\text{D}} = 410$ nm). The radiation-induced products and intermediates were characterized by FTIR and EPR spectroscopy. The structures, energetics, harmonic frequencies, hyperfine coupling constants, and isomerization pathways for several most important $\text{H}_2\text{C}_3\text{O}^{+\bullet}$ isomers were calculated at the UCCSD(T) level of theory.

The complimentary FTIR and EPR studies in argon matrices at 5 K supported by the high-level ab initio calculations have demonstrated^{3,4} that ionized $\text{C}_2\text{H}_2\cdots\text{CO}$ complex transforms into the E-HCCHCO⁺ isomer and this latter species is supposed to be the key intermediate in further chemical transformations providing a remarkable piece of evidence for kinetic control in the low-temperature chemistry. Photolysis of this species at $\lambda = 410\text{--}465$ nm results in its transformation to the thermodynamically most stable $\text{H}_2\text{CCCO}^{+\bullet}$ isomer. Possible implications of the results and potentiality of the proposed synthetic strategy to the preparation of highly reactive organic radical cations are discussed.

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