

Photochemistry of Isothiazole Isolated in Solid Ar Matrices

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Isothiazole is one of the fundamental heterocyclic molecules having a five membered ring with two hetero atoms (S and N) at adjacent positions. Those rings are rarely observed in natural products, but isothiazole derivatives can be used as effective drugs and agrochemicals because isothiazole moiety have high biological activity. For photochemical reaction, it is known that isothiazole is converted to thiazole, an isomer of isothiazole, by photoirradiation in liquid phase, while thiazole produced no products^{1,2}. Recently, UV-induced photochemistry of thiazole has been investigated by matrix-isolation FT-IR spectroscopy with a joint use of the density-functional-theory (DFT) calculations. As result, four newly recognized isocyano compounds and ethynyl compounds are produced by photochemical reaction upon UV irradiation³. The photodecomposition products of thiazole ($\text{HC}\equiv\text{N}$, $\text{HSC}\equiv\text{CH}$, $\text{H}_2\text{C}=\text{C}=\text{S}$, $\text{HC}\equiv\text{CH}$, $\text{HSC}\equiv\text{N}$, and $\text{HN}=\text{C}=\text{S}$) are also detected³. In the separate experiment using high-power UV-radiation, three types complexes of hydrogen-bonded between $\text{HS}-\text{C}\equiv\text{CH}$ and $\text{HC}\equiv\text{N}$, and other small photoproducts were reported⁴. The photochemical reaction of isothiazole isolated in low-temperature matrices is reported by Krantz et. al⁵, however they used isothiazole as precursor of thiirene, the detailed photochemical reaction of matrix-isolated isothiazole has not been reported yet. In this study, the photochemistry of isothiazole isolated in solid argon matrices is investigated using infrared spectroscopy and DFT calculations.

The isothiazole/Ar mixed gas was condensed on the cold substrate (CsI) cooled down to 18K by a closed-cycle Gifford-McMahon refrigerator. After deposition, the matrix sample was cooled down to 11K, then IR spectra of it was recorded before and after irradiation. A super-high-pressure mercury lamp (SHPML) was used to induce photochemical reaction. After irradiation using SHPML, we observed the bands at 3313, 3303, and 3232 cm^{-1} assignable to $\text{HC}\equiv\text{CSH}$, $\text{HC}\equiv\text{N}$, and $\text{HC}\equiv\text{CH}$, respectively with decreasing of the isothiazole bands at 3095 and 3061 cm^{-1} . In addition, the band of thiirene was observed at 3166 cm^{-1} , but the thiazole bands³ were not observed in this experimental condition, therefore, we concluded that the photodecomposition process of isothiazole has been progressed by UV-irradiation. We will discuss the photochemical mechanism of isothiazole isolated in solid argon matrices. This research is partly supported by the Research Institute for Science and Technology, Tokyo Denki University (Grant No: Q21K-02).

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