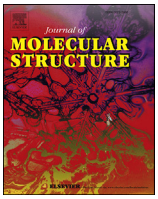
Journal of Molecular Structure 1175 (2019) 900–905

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Hydrogen-bonded complexes of ethynethiol and hydrogen cyanide trapped in low-temperature argon matrices

Jun Miyazaki [a, *], Takahiro Hatayama [b], Nobuyuki Akai [b], Munetaka Nakata [b, **]

[a] Faculty of Pharmaceutical Sciences, Hokuriku University, Ho-3, Kanagawa-machi, Kanazawa, Ishikawa, 920-1181, Japan
[b] Graduate School of BASE (Bio-Applications and Systems Engineering), Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo, 184-8588, Japan

ARTICLE INFO

Article history:
Received 21 July 2018
Received in revised form
8 August 2018
Accepted 9 August 2018
Available online 10 August 2018

Keywords:
Matrix-isolation
Hydrogen-bonded complexes
Photochemistry
Thiazole
Infrared spectroscopy
DFT calculations

ABSTRACT

Hydrogen bonding is one of the exciting and interesting research themes because it plays important roles in biomolecules, plant cells, and so on. Here we report hydrogen-bonded complexes among the photodecomposition products of thiazole, being studied by a joint use of infrared (IR) spectroscopy and density-functional-theory (DFT) calculations. Three types of hydrogen-bonded complexes of ethynethiol ($HS{-}C{\equiv}CH$) and hydrogen cyanide ($HC{\equiv}N$), which are photodecomposed by two cleavages of the NC−SC and CN−CC single bonds of thiazole in argon matrices, have been identified by comparison of the observed IR spectra with the corresponding calculated spectral patterns. In addition, another complex with weak interaction between S atom and $HC{\equiv}N$, which are photoproduced by cleavages of the three single bonds of thiazole, is detected by comparison with the wavenumbers previously reported in literature. The reaction mechanisms to form these complexes are discussed based on the analysis of IR spectra and the DFT calculations.

1. Introduction

Thiazole is a fundamental heterocyclic compound involving one S atom and one N atom in the ring. Experimental evidence of photo-induced chemical reaction of this molecule was unknown except for the photo-decomposition to cyano radical or thiocyanate radical [1], or the photo-conversion from isothiazole to thiazole [2]. Recently, UV-induced photochemical reaction of thiazole has been investigated by matrix-isolation FT-IR spectroscopy with a joint use of the density-functional-theory (DFT) calculations, resulting in the elucidation of photochemical reaction mechanisms involving the formation of newly recognized four isocyano compounds or ethynyl compounds such as *syn-N*-ethynylthioformamide ($HC{\equiv}C{-}N{-}H{-}CH{=}S$; denoted by *syn*-**6**) yielded via a biradical intermediate by cleavage of the S1−C5 bond upon UV irradiation (Scheme 1) [3]. In addition, hydrogen cyanide ($HC{\equiv}N$), ethynethiol ($HS{-}C{\equiv}CH$), ethenethione ($H_2C{=}C{=}S$), acetylene ($HC{\equiv}CH$), thiocyanic acid ($HS{-}C{\equiv}N$), and isothiocyanic acid ($HN{=}C{=}S$) are also detected as photodecomposition products by cleavages of the S1−C2, N3−C4 and/or S1−C5 single bonds (Scheme 1) [3].

The matrix-isolation technique is powerful to study atoms, molecules and clusters that are unstable in ordinary temperature and pressure conditions, because they are isolated and trapped in low-temperature inert matrices such as rare-gas solids. Thus, species with weak interactions, such as van der Waals clusters or hydrogen-bonded complexes, could be suitable targets to be investigated [4–6]. In the present study, we focus on the formation of complexes with/without hydrogen-bonding among photodecomposition products of thiazole in solid argon matrices, and discuss the stability and reactivity of these complexes by a joint use of matrix-isolation FT-IR spectroscopy and DFT calculations.

2. Experimental section

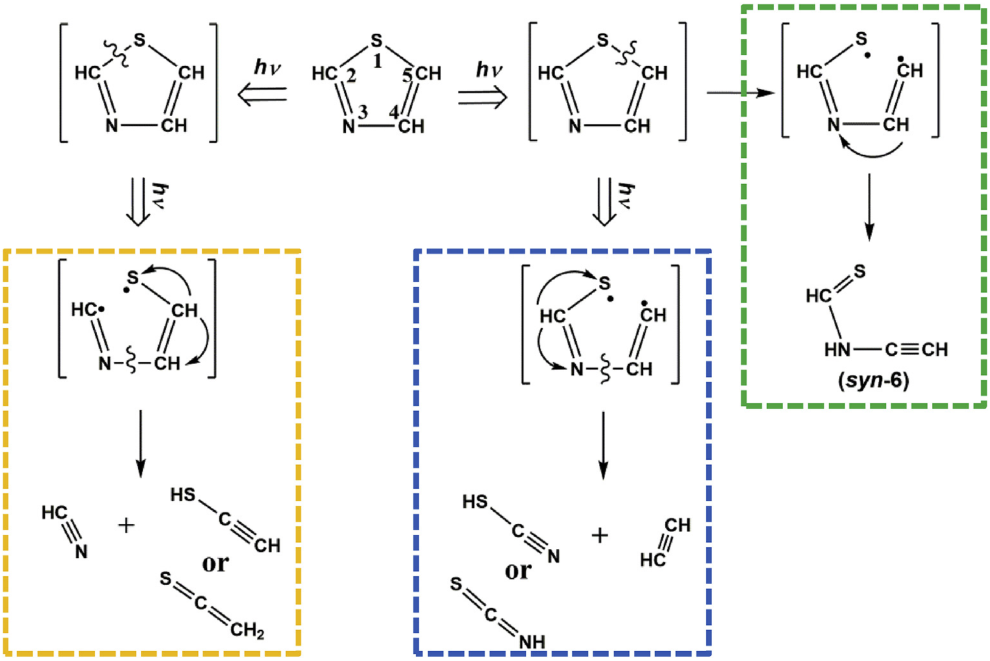
2.1. Matrix-isolation IR studies

The experimental setup is reported in our previous paper [3]. Briefly, the sample of thiazole (Tokyo Chemical Industry Co., Ltd., more than 98.0% purity) was degassed and purified by freeze-thaw cycles at 77 K and room temperature before using. Argon gas was used without further purification (99.9999% purity). The mixed gas

---

* Corresponding author.
** Corresponding author.
E-mail addresses: j-miyazaki@hokuriku-u.ac.jp (J. Miyazaki), necom816@cc.tuat.ac.jp (M. Nakata).

https://doi.org/10.1016/j.molstruc.2018.08.028



Scheme 1. A part of photoreaction and photodecomposition pathways of thiazole [3].

of thiazole and argon, which was prepared in a gas line at room temperature, was condensed on a CsI plate cooled to 20 K by a closed-cycle He refrigerator (CTI, Cryogenics, M-22) over a period of 40–70 min so as to show good signal-to-noise IR spectra.

Infrared spectra were recorded with an FT-IR spectrometer (JEOL, JIR-7000) equipped with an MCT detector cooled by liquid N_2. All the spectra were measured at 0.5 cm^{-1} resolution and averaged over 100 scans. UV–vis radiation from a super high-pressure mercury lamp (SHPML) with a power of 500 W (USHIO, HB-50106AA-A) was used to induce photoreaction, where a water filter was used to avoid thermal reactions.

2.2. Computational method

The GAUSSIAN03 program package was used for all calculations [7]. Geometry optimization and frequency analysis were performed by DFT calculations at the UB3LYP level using aug-cc-pVTZ basis set in order to obtain IR spectral patterns of thiazole, hydrogen-bonded complexes, and photodecomposition products of thiazole. Scaling factors of 0.96, 0.97 and 0.98 were applied to the regions over 2800 cm^{-1}, between 2800 and 1900 cm^{-1}, and below 1900 cm^{-1}, respectively.

3. Results and discussions

The IR spectral regions of C–H and S–H stretching modes for the photoproducts of thiazole isolated in low-temperature argon matrices are shown in Figs. 1 and 2, respectively. As reported in our previous paper [3], some IR bands in these spectral regions have been assigned to the photoproducts having C–H and/or S–H bonds; *syn-N*-ethynylthioformamide (*syn*-**6**) produced from thiazole by cleavage of the S1–C5 single bond with hydrogen-atom migration from C4 to N3 to generate the C=S double bond (see the green area of Scheme 1), ethynethiol (HS–C≡CH) and hydrogen cyanide (HC≡N) by two cleavages of the S1–C2 and N3–C4 single bonds with hydrogen-atom migration (see the orange area of Scheme 1), and acetylene (HC≡CH) by two cleavages

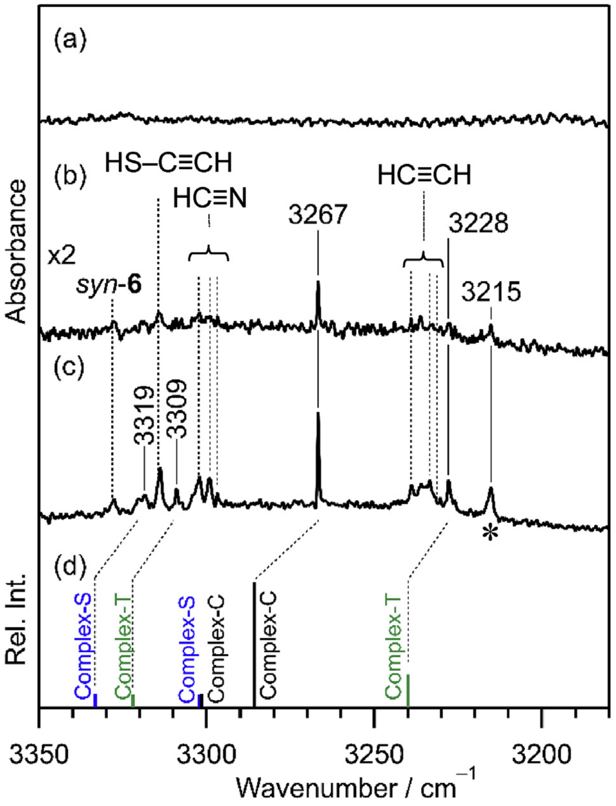


Fig. 1. IR spectra in the C–H stretching region: Observed spectrum of thiazole in argon matrices (a); Difference IR spectra between the spectra measured before and after UV irradiation for 4 min (b) and 18 min (c). The absorbance of (b) is multiplied by a factor of 2. *Syn*–**6** denotes *syn-N*-ethynylthioformamide (Ref. in [3]). The symbol of * denotes S···HC≡N complex; Calculated spectral patterns of HS–C≡CH···N≡CH (Complex-C) (black), HC≡N···HS–C≡CH (Complex-S) (blue), and N≡CH···CH≡CH–SH (Complex-T) (green) at the DFT/UB3LYP/aug-cc-pVTZ level (d). A scaling factor of 0.96 is applied. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)